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CONTROL TECHNIQUES FOR NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES

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U. S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Environmental Health Service

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CONTROL TECHNIQUES FOR NITROGEN OXIDES FROM STATIONARY SOURCES

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Environmental Health Service
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PREFACE

Throughout the development of Federal air pollution legislation, the Congress has consistently found that the States and local governments have the primary responsibility for preventing and controlling air pollution at its source. Further, the Congress has consistently declared that it is the responsibility of the Federal government to provide technical and financial assistance to State and local governments so that they can undertake these responsibilities.

These principles were reiterated in the 1967 amendments to the Clean Air Act. A key element of that Act directs the Secretary of Health, Education, and Welfare to collect and make available information on all aspects of air pollution and its control. Under the Act, the issuance of control techniques information is a vital step in a program designed to assist the States in taking responsible technological, social, and political action to protect the public from the adverse effects of air pollution.

Briefly, the Act calls for the Secretary of Health, Education, and Welfare to define the broad atmospheric areas of the Nation in which climate, meteorology, and topography, all of which influence the capacity of air to dilute and disperse pollution, are generally homogeneous.

Further, the Act requires the Secretary to define those geographical regions in the country where air pollution is a problem—whether interstate or intrastate. These air quality control regions are designated on the basis of meteorological, social, and political factors which suggest that a group of communities should be treated as a unit for setting limitations on concentrations of atmospheric pollutants. Concurrently, the Secretary is required to issue air quality criteria for those pollutants he believes may be harmful to health or welfare, and to publish related information on the techniques which can be employed to control the sources of those pollutants.

Once these steps have been taken for any region, and for any pollutant or combination of pollutants, then the State or States responsible for the designated region are on notice to develop ambient air quality standards applicable to the region for the pollutants involved, and to develop plans of action for meeting the standards.

The Department of Health, Education, and Welfare will review, evaluate, and approve these standards and plans and, once they are approved, the States will be expected to take action to control pollution sources in the manner outlined in their plans.

At the direction of the Secretary, the National Air Pollution Control Administration has established appropriate programs to carry out the several Federal responsibilities specified in the legislation.

Control Techniques for Nitrogen Oxides from Stationary Sources is one of a series of documents to be produced under the program established to carry out the responsibility for developing and distributing control technology information. Previously, on February 11, 1969, control technique information was published for sulfur oxides and particulate matter.

In accordance with the Clean Air Act, a National Air Pollution Control Techniques Advisory Committee was established, having a membership broadly representative of industry, universities, and all levels of government. The committee, whose members are listed following this discussion, provided invaluable advice in identifying the best possible methods for controlling the pollution sources, assisted in determining the costs involved, and gave major assistance in drafting this document.

As further required by the Act, appropriate Federal departments and agencies, also listed on the following pages, were consulted prior to issuance of this document. A Federal consultation committee, comprising members designated by the heads of 17 departments and agencies, reviewed the document, and met with staff personnel of the National Air Pollution Control Administration to discuss its contents.

During 1967, at the initiation of the Secretary of Health, Education, and Welfare, several government-industry task groups were formed to explore mutual problems relating to air pollution control. One of these, a task group on control technology research and development, looked into ways that industry representatives could participate in the review of the control techniques reports. Accordingly, several industrial representatives, listed on the following pages, reviewed this document and provided helpful comments and suggestions. In addition, certain consultants to the National Air Pollution Control Administration also revised and assisted in preparing portions of this document. These also are listed on the following pages.

The Administration is pleased to acknowledge efforts of each of the persons specifically named, as well as those of the many not so listed who contributed to the publication of this volume. In the last analysis, however, the National Air Pollution Control Administration is responsible for its content.

The control of air pollutant emissions is a complex problem because of the variety of sources and source characteristics. Technical factors frequently make necessary the use of different control procedures for different types of sources. Many techniques are still in the development stage, and prudent control strategy may call for the use of interim methods until these techniques are perfected. Thus, we can expect that we will continue to improve, refine, and periodically revise the control techniques information so that it will continue to reflect the most up-to-date knowledge available.

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TABLE OF CONTENTS

Section *Page*

LIST OF TABLES xi

LIST OF FIGURES xii

SUMMARY xiv

1. INTRODUCTION 1-1

2. DEFINITIONS 2-1

  2.1 REFERENCES FOR SECTION 2 2-2

3. SOURCES OF NITROGEN OXIDES 3-1

  3.1 REFERENCES FOR SECTION 3 3-5

4. COMBUSTION CONTROL TECHNIQUES 4-1

  4.1 COMBUSTION MODIFICATIONS 4-1

    4.1.1 Factors Affecting NO_x Emissions 4-3

      4.1.1.1 Fuel Type and Composition 4-4

      4.1.1.2 Heat Release and Transfer Rates 4-4

    4.1.2 Modifications of Operating Conditions 4-5

      4.1.2.1 Low Excess Air Combustion 4-5

      4.1.2.2 Flue Gas Recirculation 4-6

      4.1.2.3 Steam and Water Injection 4-7

    4.1.3 Design Modifications 4-8

      4.1.3.1 Burner Configuration 4-8

      4.1.3.2 Burner Location and Spacing 4-8

      4.1.3.3 Fluidized Bed Combustion 4-9

      4.1.3.4 Small Combustion Equipment 4-11

  4.2 FLUE GAS CLEANING 4-11

    4.2.1 Control by Limestone Wet-Scrubbing Process 4-11

    4.2.2 Potential Control Processes 4-13

      4.2.2.1 Reinluft Char Process 4-13

      4.2.2.2 Control by Tyco Laboratories' Modified Lead Chamber Process 4-13

  4.3 REFERENCES FOR SECTION 4 4-14

5. LARGE FOSSIL FUEL COMBUSTION PROCESSES 5-1

  5.1 ELECTRIC POWER PLANT BOILERS 5-1

    5.1.1 Emissions 5-1

    5.1.2 Control Techniques 5-1

      5.1.2.1 Conversion to Lower NO_x Producing Fuel 5-1

      5.1.2.2 Fuel Additives 5-2

      5.2.2.3 Combustion Control 5-2

    5.1.3 Costs 5-3

      5.1.3.1 Limitations with Large Coal-Fired Boilers 5-4

      5.1.3.2 Packaged Boilers 5-4

  5.2 STATIONARY ENGINES 5-5

Section *Page*

5.2.1 Piston Engines 5-5
5.2.1.1 Emissions 5-6
5.2.1.2 Control Techniques 5-6
5.2.2 Turbine Engines 5-9
5.2.2.1 Emissions 5-9
5.2.2.2 Control Techniques 5-9
5.2.3 Costs 5-10
5.2.3.1 Diesel Engines 5-10
5.2.3.2 Gas Engines 5-11
5.3 REFERENCES FOR SECTION 5 5-11
6. OTHER COMBUSTION PROCESSES 6-1
6.1 DOMESTIC AND COMMERCIAL HEATING 6-1
6.1.1 Emissions 6-2
6.1.2 Control Techniques 6-2
6.2 INCINERATION AND OTHER BURNING 6-3
6.2.1 Emissions 6-3
6.2.2 Control Techniques 6-4
6.2.2.1 Waste Disposal 6-4
6.2.2.2 Forest Wildfires 6-5
6.2.2.3 Controlled Vegetation Burning 6-5
6.2.2.4 Coal Refuse Fires 6-6
6.2.2.5 Structural Fires 6-6
6.2.3 Costs of Control 6-6
6.3 REFERENCES FOR SECTION 6 6-6
7. INDUSTRIAL AND CHEMICAL PROCESSES 7-1
7.1 NITRIC ACID MANUFACTURE 7-2
7.1.1 Emissions 7-4
7.1.2 Control Techniques 7-5
7.1.3 Costs for Control 7-9
7.2 NITRIC ACID USES 7-11
7.2.1 Ammonium Nitrate Manufacture 7-12
7.2.1.1 Emissions 7-12
7.2.2 Organic Oxidations 7-12
7.2.2.1 Emissions 7-13
7.2.2.2 Control Techniques 7-13
7.2.2.3 Costs of Control 7-14
7.2.3 Organic Nitrations 7-14
7.2.3.1 Emissions from Nitration 7-20
7.2.3.2 Control Techniques 7-20
7.2.3.3 Costs of Controls 7-21
7.2.4 Explosives: Manufacture and Use 7-21
7.2.4.1 Emissions 7-23
7.2.5 Other Uses of Nitric Acid 7-24
7.2.5.1 Fertilizer 7-24
7.2.5.2 Metals Pickling 7-25
7.3 PETROLEUM AND NATURAL GAS INDUSTRIES 7-25
7.3.1 Emissions 7-26

Section *Page*

7.3.2 Control Techniques 7-31
7.3.3 Costs of Control 7-32
7.4 METALLURGICAL PROCESSES 7-32
7.4.1 Furnaces Related to Hot Metal or Pig Iron Production 7-32
7.4.1.1 Blast Furnace 7-32
7.4.1.2 Blast Furnace Stove 7-33
7.4.2 Furnaces Related to Steel Production 7-34
7.4.2.1 Open Hearth Furnace 7-34
7.4.2.2 Coking Ovens 7-34
7.4.2.3 Miscellaneous Furnaces 7-35
7.4.3 Emissions 7-36
7.4.4 Costs 7-37
7.5 KILNS - CEMENT, LIMESTONE, AND CERAMICS 7-37
7.5.1 Emissions 7-38
7.5.2 Control Techniques 7-39
7.6 GLASS MANUFACTURE 7-39
7.6.1 Emissions 7-41
7.6.2 Control Techniques 7-41
7.7 MISCELLANEOUS NO_x EMISSION SOURCES 7-42
7.7.1 Process Description 7-42
7.7.1.1 Refractory Fibers 7-42
7.7.1.2 Perlite Expanding Furnaces 7-42
7.7.1.3 Baking and Drying Ovens 7-42
7.7.1.4 Spray Dryers 7-42
7.7.1.5 Welding 7-42
7.7.1.6 Electrostatic Precipitators 7-43
7.7.1.7 High-Level Exposure in Agriculture 7-43
7.7.2 Control Techniques 7-43
7.8 REFERENCES FOR SECTION 7 7-44
8. NITROGEN OXIDES EMISSION FACTORS 8-1
8.1 EMISSION FACTOR ACCURACY 8-1
8.2 REFERENCES FOR SECTION 8 8-4
9. POSSIBLE NEW TECHNOLOGY 9-1
9.1 POTENTIAL COMBUSTION MODIFICATIONS 9-1
9.1.1 Oxygen Enrichment 9-1
9.1.2 Fluid Bed Combustion 9-1
9.1.3 Centralization of Energy Source 9-1
9.2 FLUE GAS REMOVAL 9-2
9.2.1 Improved Aqueous Scrubbing 9-2
9.3 REFERENCES FOR SECTION 9 9-2
SUBJECT INDEX I-1

LIST OF TABLES

Table *Page*

3-1. Time for NO Formation in a Gas Containing 75 Percent Nitrogen and 3 Percent Oxygen 3-1
3-2. Estimates of Nitrogen Oxide Emissions in the United States, by Source, 1968. 3-2

Table *Page*

3-3. Comparison of Coal, Oil, and Gas on Equivalent Btu Basis. 3-4
4-1. Calculated Equilibrium Concentration of Nitrogen Oxides 4-2
4-2. Typical Compositions and Solubility of Stack Gases. 4-12
5-1. Estimated Control Costs and Reduction of NO_x Emissions, for a 1,000-Megawatt Boiler Used 6,120 Hours a Year, by Selected Methods and by Ton. 5-3
5-2. Stationary Reciprocating Piston Engines in United States, 1967. 5-5
5-3. Estimated Stationary Engine Distribution in United States, 1969. 5-6
5-4. Summary of Source Sampling Tests for Two Dual-Fuel (Gas and Diesel) Engines. 5-7
5-5. Effect of Fuel Type on Emissions of NO_x from a Stationary Diesel Engine. . 5-8
5-6. Effect of Air/Fuel Ratio on NO_x Production in Spark-Ignited Stationary Gas Engines. 5-8
5-7. Effect of Air/Fuel Ratio on NO_x Formation in an Experimental Combustor Rig. 5-10
5-8. Oxides of Nitrogen Control Costs for Stationary Gas Engines. 5-11
6-1. Fuel Consumption for Space Heating and Cooking, 1966. 6-1
6-2. Gas Consumption for Domestic Heating in United States. 6-1
6-3. Estimated National Emissions from Incineration and Other Burning, 1968. . 6-4
7-1. Estimates of Strong Acid Requirements and Oxides of Nitrogen Emissions from Concentration Operations. 7-5
7-2. Estimated Costs of Catalytic Reduction for Three Control Systems. 7-10
7-3. Estimated Nitric Acid Consumption in United States, 1967. 7-11
7-4. Estimated Acid Requirements and Oxides of Nitrogen Emissions from Nitric Acid Oxidation of Organic Compounds, 1967. 7-14
7-5. Estimated Oxides of Nitrogen Emissions from Organic Nitrations, 1967. . . 7-20
7-6. Ingredients in U.S. Industrial Explosives, 1967. 7-21
7-7. Total United States Nitric Acid Requirements and Oxides of Nitrogen Emissions from the Manufacture of Industrial Explosives, 1967 7-23
7-8. Oxides of Nitrogen in Products of Explosions. 7-24
7-9. NO_x Emissions from Petroleum and Natural Gas Operations, 1967. 7-29
7-10. Nitrogen Oxides Emissions from Petroleum and Natural Gas Operations in United States,1967. 7-31
7-11. Investment Cost Estimates for Refinery Furnaces in Two Sizes, at a Standard Location, with Oxides of Nitrogen Control by Flue Gas Recirculation, April-June 1969 7-33
7-12. Fuel Consumed by Cement Industry in United States, 1967 7-37
7-13. Estimated Oxides of Nitrogen Emissions from Kilns in United States, 1967. . 7-38
8-1. Emission Factors for Nitrogen Oxides During Combustion of Fuels and Other Materials. 8-3

LIST OF FIGURES

Figure *Page*

3-1. Total Estimated Oxides of Nitrogen Emissions from Mobile and Stationary Sources in United States (20,669,000 tons), by Fuel Type and Tonnage, 1968. 3-3
3-2. Total Estimated Oxides of Nitrogen Emissions from Stationary Installations in United States (9,600,000 tons), by Type of Use and Tonnage, 1968. . . . 3-4

Figure *Page*

4-1. Calculated Nitric Oxide Concentration from Oil- and Gas-Firing, 0.5 sec. Residence Time Excess Air. 4-3
4-2. Effect of Heat Release of Oxides of Nitrogen Emissions, by Type of Firing . 4-4
4-3. Effect of Excess of Air on Oxides of Nitrogen Emissions from Oil-Fired Boilers. 4-5
4-4. Oxides of Nitrogen Emissions from Oil-Fired Boilers at Low Excess Air . . . 4-6
4-5. Combined Effect of Flue Gas Recirculation and Excess Air on Oxides of Nitrogen Emissions from an Oil-Fired Domestic Heating Furnace. 4-7
4-6. Multi-Fuel Burner for Gas (Spud-Type Burner), Oil (Circular Register), and Coal (Circular Register). 4-9
4-7. Gas-Ring Type Burner. 4-10
4-8. Limestone Injection Wet-Scrubbing Process. 4-13
4-9. Flow Diagram for Tyco Process. 4-14
7-1. Flow Diagram of a Typical 120-Ton-per-Day Nitric Acid Plant Utilizing the Pressure Process. 7-3
7-2. Nitric Acid Concentrating Unit. 7-4
7-3. Adipic Acid Synthesis. 7-12
7-4. Terephthalic Acid Synthesis. 7-13
7-5. Batch Process for the Manufacture of Nitroglycerin 7-16
7-6. Schmid-Meissner Continuous-Nitration Plant 7-17
7-7. Biazzi Continuous Nitration Plant 7-18
7-8. Recovery of Spent Acid. 7-19
7-9. TNT Manufacturing Diagram. 7-22
7-10. Composite Processing Plan for a Modern Refinery. 7-27
7-11. Fluidized Bed Catalytic Cracking Unit (FCC). 7-28
7-12. Oxides of Nitrogen Emissions from Refinery Furnace 7-30
7-13. Variation in Oxides of Nitrogen Emission Rates from Stationary Internal Combustion Figures. 7-31
7-14. Regenerative Side Port Glass-Melting Furnace. 7-40
8-1. Estimation of Average Unit Oxides of Nitrogen Emissions from Similar Combustion Equipment 8-2

SUMMARY

DEFINITION

In this document, the term "nitrogen oxides" or "NO_x" refers to either or both of two gaseous oxides of nitrogen, nitric oxide (NO) and nitrogen dioxide (NO_2). These substances are important in air pollution control because they are involved in photochemical reactions in the atmosphere and because, by themselves, they have undesirable physiological effects.

FACTORS INFLUENCING NO_X FORMATION

Chemical Equilibrium

Under proper conditions, nitrogen and oxygen tend to combine in accordance with the following equation:

$$N_2 + O_2 \leftrightarrows 2\ NO$$

The equilibrium concentration of NO varies with temperature; it is negligible below 1,000° F but quite significant above 3,000° F. In addition, it is influenced by gas composition; at a given temperature, for example, the equilibrium concentration of NO in air exceeds that of NO in a flue gas of 3 percent oxygen content by a factor of approximately 3.

Nitric oxide tends to react with oxygen as follows:

$$NO + 1/2\ O_2 \leftrightarrows NO_2$$

This equation implies the coexistence of NO and NO_2. Calculated equilibria indicate that the stability of NO_2 decreases with increasing temperature. Nevertheless, from an equilibrium standpoint, the absolute concentration of NO_2 increases with temperature while the ratio of its concentration to that of NO decreases with increasing temperature.

Chemical equilibria depend only on the initial and final states and not at all on reaction mechanisms or intermediate reaction steps. Equilibrium concentrations are obtained after the lapse of sufficient reaction time; therefore, they are not necessarily observed experimentally. Because of the simplicity of the molecules involved in the foregoing equations, their thermodynamic properties are accurately known and equilibrium calculations are made easily. Such calculations serve as an estimate for emission quantities and as a guide in equipment design.

Rates of Formation

Rates of formation can be calculated by kinetic equations that depend heavily on experimental measurements. The products obtained depend in large measure on the relative speeds of the reactions that actually occur. The rate of oxidation of nitrogen to NO is highly temperature-dependent; it is very slow at 500° F, but fast at 4,000° F. The underlying reason is that a high level of energy is needed to break the N-N bond of molecular nitrogen so that oxygen can react. Conversely, a smaller but still relatively great amount of energy is needed to break the N-O bond to permit decomposition of nitric oxide into its elements. This means that high temperatures are required to form NO; once formed, it resists any breakdown into its elements. Breakdown becomes more and more unlikely as temperature decreases, because the energy available for thermal breakdown diminishes rapidly with decreasing temperature. Thus, an initially high temperature followed by quick cooling, even to a relatively high temperature level, produces large amounts of NO.

At temperatures above 2,000°F, both NO and NO_2 are formed, but the amount of NO_2

is usually well under 0.5 percent of the total NO_x. The oxidation of NO to NO_2 by oxygen, however, is peculiar in that its rate of formation decreases with increasing temperature. This is one of the few known reactions that exhibit such a decrease. The resultant slow oxidation rate at high temperatures accounts in part for the negligible amounts of NO_2 frequently found in hot combustion gases. Another characteristic of the oxidation of NO to NO_2 by oxygen only, is the fact that the rate varies with the square of the NO concentration. The rate of oxidation of NO by oxygen in air falls off rapidly, therefore, with dilution of the NO. A long period of time may be required to oxidize trace quantities of NO by this mechanism, but photochemical reaction in sunlight accomplishes such oxidation in a much shorter time.

As in all chemical reactions, the rates of formation and decomposition for NO and NO_2 can be hastened by means of catalysts. Attainable theoretical equilibrium concentrations are not changed by catalysts; only the time of attainment is changed. With or without a catalyst, equilibrium concentrations may be approached when either a high or low NO_x concentration is present.

SOURCES

Mobile sources, the largest single source category, contribute over 40 percent of all the man-made NO_x emitted in the United States. Current knowledge on methods of control is covered in detail in AP-66, *Control Techniques for Carbon Monoxide, Nitrogen Oxide, and Hydrocarbon Emissions from Mobile Sources.* The next largest source is electric power generation, which is responsible for nearly 20 percent of all man-made NO_x. About 40 percent of NO_x emitted from stationary installations is attributed to electric-generating power plants.

About 1 percent of the total man-made NO_x emitted to the ambient air of the United States is formed by chemical sources, mainly related to the manufacture and use of nitric acid. Concentrations from these sources are, however, usually much greater than those from noncombustion sources, and, therefore, often give rise to a highly visible, brown-red gas.

CONTROL TECHNIQUES – COMMERCIALLY DEMONSTRATED

Combustion Modifications

Two-stage combustion in oil- and gas-fired boilers has reduced NO_x emissions from power plant boilers by 30 to 50 percent. Low-excess-air operation has reduced NO_x emissions from oil- and gas-fired power plant boilers by 30 to 60 percent, depending upon the percentage of excess air, the design of the boiler, and the type of firing. By changing the firing of power plant boilers from front-wall, or opposed, firing to tangential firing, NO_x has been reduced from 30 to 40 percent.

A modified two-stage combustion technique, combined with low-excess-air firing has reduced the stack-gas NO_x concentration emitted by two 750-megawatt gas-fired power-plant boilers from 1,500 to 175 parts per million (ppm). Nominal costs were reported by the company with no decrease in generating capacity.

All of the above approaches are based on considerations of chemical equilibrium and reaction rate. They involve reduction of peak gas temperatures, trends away from oxidizing and toward reducing atmospheres, and changes in the time-temperature history of the combustion gases. These approaches are all commercially demonstrated for large oil- and gas-fired boilers, but are yet to be demonstrated for large coal-fired boilers.

Changes in Fuel or Energy Source

Generation of electricity through the use of nuclear energy is projected to grow in the future. Essentially, no nitrogen oxides are emitted since this source of energy does not depend on the combustion of fossil fuels. In 1968, 12 billion kilowatt-hours of electric power generated from nuclear energy was reported in the United States; reliable sources project 3,000 billion kilowatt-hours by 1990.

Waste Disposal

Substitution of sanitary landfills for open burning has proved to be a commercially demonstrated control technique in certain areas of the country.

Chemical Sources

Chemical vent gases normally are much more highly concentrated than combustion gases, and the NO content can be more quickly oxidized by oxygen in air. If uncontrolled, these streams of NO_x may create air pollution problems when relatively high ground-level concentrations occur.

Nitrogen oxides from chemical sources may be decolorized by catalytic reduction using fuels, such as natural gas or hydrogen. Such reactions are exothermic and much heat is generated. Because of practical considerations, such as catalyst life and the temperature limitations of structural materials, only the process of decolorization by reduction to NO has been uniformly successful.

Catalytic reduction of NO_2 to NO is not a true control technique; it merely decolorizes the stack gas. Stack velocities and normal atmospheric turbulence contribute to rapid dilution, with increasingly slow rates of oxidation of NO by air. Photochemical reactions in the atmosphere can, however, oxidize these small NO concentrations to NO_2.

CONTROL TECHNIQUES - VARIED COMMERCIAL SUCCESS

Energy Substitution

Industrial, commercial, and household thermal requirements contribute to above-average NO_x concentrations in urban areas. These thermal requirements may be met in part by central electric-power stations with adequate NO_x emission controls. Emissions of NO_x are easier to control from such a large centrally located complex. The efficiency of a heating system, however, is lower when conversion of fuel to electricity to heat is required than it is when the system is designed to convert fuel to heat directly.

Source Relocation

Relocation of a pollutant source is a means of reducing the exposure of a densely populated area to NO_x emissions. Such a plan entails retirement of the old urban electricity-generating stations and the building of new, more efficient, power-generating stations at remote locations.* Economic feasibility may be affected, however, by the cost of long-distance power transmission.

Catalytic Abatement

Catalytic abatement is similar to catalytic decolorization, but the NO_x is reduced completely to elemental nitrogen. In catalytic abatement of NO_x, sufficient fuel is used to give complete oxygen burnout, followed by reduction of NO_x to elemental nitrogen. Difficulties in applying this principle in commercial practice have included short catalyst life and high-temperature problems. Low initial oxygen content in the gas to be treated is recommended.

Caustic Scrubbing

Solutions or suspensions of caustic or calcium hydroxide react with NO_2 and with equimolar ratios of NO and NO_2. The latter mixtures are absorbed to form nitrites, just as if they were the actual anhydride of nitrous acid, N_2O_3. It follows that scrubbers can be designed for a high degree of removal of NO_x from chemical vent streams. When scrubbers are used, a solution of nitrate and nitrite is formed. If no use is made of the solution on site, it can create a waste-disposal problem. Also, the nitrite can decompose to regenerate NO_x if the waste is dispersed into a lower-pH environment. NO_x removal by means of scrubbers may not, therefore, be desirable.

Nitrogen Oxide Incineration

Nitrogen oxide incineration involves reduction of NO_x to elemental nitrogen by burnout with a gaseous fuel. This differs from catalytic abatement in that no catalyst is used. At least 10 percent more fuel than required for reaction with oxygen and NO_x is added to the vent gas stream to reduce NO_x

to nitrogen. NO_X reductions of 75 to 90 percent have been obtained. Because of the reducing (fuel rich) conditions employed, CO and HC may be present in the exit gas, and more air and a second reactor may be required to control these pollutants.

The NO_X incineration method might be useful for treatment of nitric acid absorber tail gas following commercial nitration operations.

Urea Inhibition of Nitrogen Oxides

In some cases where strong nitric acid solutions are used, urea can be added to inhibit or prevent release of NO_X. This method has been used in metal pickling, in phosphate rock acidulation, and in some nitrations.

CONTROL TECHNIQUES (SPECULATIVE)

Steam and Water Injection

A potential control technique, steam and water injection, is based on lowering the boiler peak flame temperature and diluting the combustion gases, as in flue-gas recirculation. This method requires development and may involve loss in efficiency, but it has been found to reduce NO_X emissions from internal combustion engines.

Flue-Gas Recirculation

Laboratory results of the flue-gas recirculation technique show sizable reductions in NO_X emissions, particularly in combination with low-excess-air firing, but tests on boiler emissions are inconclusive. The recirculated flue gases should be injected directly into the flame zone.

Stack-Gas Treatment

Several treatments are under development for removal of sulfur oxides from flue gases, and some of these techniques also remove a part of the NO_X content simultaneously. These treatments are described in AP-52, *Control Techniques for Sulfur Oxide Air Pollutants.* Difficulties have been encountered in operating most of these processes.

A disadvantage of flue-gas treatment of large gas volumes is that scrubbing with water cools the gases to as low as perhaps 125° F, and thereby creates a visible plume with poor buoyancy.

Selective Catalytic Reduction of NO_X

This process uses ammonia in the presence of oxygen to reduce NO_X. Limited commercial experience in three plants ranged from unsatisfactory to partially successful.

Adsorption on Molecular Sieves

Molecular sieves are solid chemical structures that can adsorb NO_X from very low concentrations in a gas stream. The adsorbed NO_X can be desorbed with hot air or steam, and the NO_X exit concentration is greatly raised over that of the entering tail-gas stream. Process units involving adsorption and desorption of NO_X on molecular sieves are offered commercially, and the degree of removal of NO_X is guaranteed. No reports of their use in an actual plant are available. Limited evidence indicates that adsorption is quite satisfactory from a well-dried gas. Some user, such as a nitric acid plant, must be located nearby to accept the concentrated NO_X gas stream resulting from the desorption step.

CONTROL TECHNIQUES FOR NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES

1. INTRODUCTION

Pursuant to authority delegated to the Commissioner of the National Air Pollution Control Administration, *Control Techniques for Nitrogen Oxide Emissions from Stationary Sources* is issued in accordance with Section 107(c) of the Clean Air Act as amended (42 U.S.C. 1857-18571).

Nitrogen oxides in the atmosphere are known to be involved in the formation of photochemical smog of the Los Angeles type through complex reactions with hydrocarbons and other pollutant gases under the influence of sunlight.

Oxides of nitrogen (NO_X) are emitted from both stationary and mobile sources, in roughly equal proportions on a nationwide basis. They are emitted in significant amounts as the result of the fixation of nitrogen in combustion processes, but not directly in proportion to the nitrogen content of fossil fuels burned.

Although control of NO_X is a complex problem, there are some NO_X sources for which control techniques are now available at relatively low cost; and, in a number of instances, promising laboratory data have indicated that other control techniques are ready for further testing and development.

Nitrogen oxides are emitted from many fossil-fuel combustion sources and, to a lesser extent, other industrial stationary sources. Fuel type, equipment operation and design, and other variables influence the levels of NO_X emitted by individual sources to the extent that currently available emission factors have only a broad and generalized applicability. A number of potential techniques being developed for controlling these emissions are based either on principles that prevent the formation of NO_X or on methods for the removal of NO_X from stack or tail gases. Except for a few chemical reactions that occur when the only reactive constituent of the tail gas is NO_X, the feasible methods appear to be confined to those that control nitrogen oxides and sulfur oxides emissions simultaneously.

Noncombustion processes contribute only a small proportion of total NO_X emissions, but can present a serious local hazard. Control technology in this area has been the subject of intensive research, particularly in the manufacture and uses of nitric acid wherein NO_2 is a process raw material. Control technology via combustion modification in oil- and gas-fired processes has been applied, and this method is recommended for further application and development. Several other potential techniques must await the results of further research and development in controlling nitrogen oxide emissions from stationary sources.

While some data are presented herein on quantities of nitrogen oxides emitted to the atmosphere, the effects upon health and welfare of nitrogen oxides and their secondary atmospheric reaction products are considered in two companion documents, AP-63, *Air Quality Criteria for Photochemical Oxidants* and *Air Quality Criteria for Nitrogen Oxides.**

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*To be issued at a later date.

2. DEFINITIONS

Two oxides of nitrogen are important in the atmosphere: nitric oxide (NO) and nitrogen dioxide (NO_2). Five more oxides of nitrogen are known: NO_3, N_2O, N_2O_3, N_2O_4, and N_2O_5. The oxides NO_3 and N_2O_4 are too unstable to exist at atmospheric conditions; N_2O_3 and N_2O_5 are the anhydrides of nitrous and nitric acid respectively; and N_2O, the anesthetic known as "laughing gas," is a stable compound and can support combustion.

The term NO_x is used generally to represent the gaseous pollutants NO_2 and NO, expressed as NO_2. It is known that NO is oxidized to NO_2 by oxidants, including oxygen in the air. Special precautions in sampling and analysis are required, therefore, to get reliable measurements of NO. This difficulty is serious enough to cast doubt on most of the data in the older literature since the ratio of NO to NO_2 may not be reliable.

Nitrous oxide (N_2O) is formed largely from the decomposition of nitrogen compounds by soil bacteria. It has a mean concentration of about 0.25 ppm in the atmosphere.[1] Nitric oxide and nitrogen dioxide are formed under high-temperature conditions such as the burning of fossil fuels, and in much larger amounts by various biological reactions in nature but in low concentrations. Most of the NO_x formed by man is nitric oxide, which is oxidized to the more toxic and irritant nitrogen dioxide by the oxygen of the air, or, much more easily, by photochemically reactive hydrocarbons in the presence of sunlight.

Two commonly used methods are available for determination of NO_x. They are the phenol-disulfonic acid method and the modified Saltzman method. Of these two, the phenol-disulfonic acid method has been used to obtain the bulk of the data on NO_x emission factors.

The phenol-disulfonic acid method for the determination of NO_x is described in the American Society for Testing Materials (ASTM) Standard Procedure D 1608.[2] It is noted in the procedure that samples not analyzed promptly will give low results; this is a common failing of older data in the literature. An important variable is the gradual chemical reduction of NO_2 to NO and, to a lesser extent, of NO to nitrogen by the action of SO_2 in the presence of H_2O, in a flue gas. The presence of other combustion effluents can also create uncertainties.

The Saltzman method for determination of NO_x is a modification[3] of the Greiss Ilosvay reaction[4] described in ASTM Standard Procedure D 1608. This method depends upon the development of a red-violet color, which can be compared to standards either visually or spectrophotometrically. The comparison should be made without delay if the sample contains oxidizing or reducing gases other than NO_x.

The accuracy of older NO_x data in the literature is suspect, unless the user is sure that the analyst allowed for the reducing effect of any SO_2 present.

Flue-gas analyses may be corrected for the dilution effect of excess air, and one method of reporting would be to recalculate the observed results to the basis of 3 percent excess oxygen. The extent of this effect can be illustrated by the example of a flue gas containing 555 ppm of NO_x at 1 percent excess oxygen; this would be calculated to be 500 ppm on the basis of sufficient air to give 3 percent O_2 in the flue gas (2 percent excess O_2 is about 10 percent excess air; calculated dilution ratio is 111:100).

2.1 REFERENCES FOR SECTION 2

1. Goody, R.M. and C.D. Walshaw. The Origin of Atmospheric Nitrous Oxide. Quart. J. Roy. Meteorol. Soc. *79*(342):496-500, October 1953.
2. Oxides of Nitrogen in Gaseous Combustion Products (Phenol-Disulfonic Acid Procedure) (ASTM Designation: D 1608-60). In: The 1968 Book of ASTM Standards, Part 23. Philadelphia, American Society for Testing and Materials, October 1968. p. 461-465.
3. Saltzman, B.E. Colorimetric Microdetermination of Nitrogen Dioxide in the Atmosphere. Anal. Chem. *26*:1949-1955, December 1954.
4. Thomas, M.D. et al. Automatic Apparatus for Determination of Nitric Oxide and Nitrogen Dioxide in the Atmosphere. Anal. Chem. *28*(12):1810-1816, 1956.

3. SOURCES OF NITROGEN OXIDES

When fossil fuels (gas, fuel oils, and coal) are burned with air, some of the oxygen and nitrogen gas present combine to form NO according to the following reaction:

$$N_2 + O_2 \leftrightarrows 2NO$$

Given time, this reaction continues to an equilibrium level, which depends upon variables such as flame temperature, the concentration of each gas, and the movement of the gases through zones of different temperatures, pressures, and concentrations. Once NO is formed, however, the rate of decomposition is very slow, too slow for NO to dissociate into oxygen and nitrogen under ordinary reaction conditions. As a result, the NO persists, or is "frozen" in the flame products after they leave the high-temperature zone. The data in Table 3-1 show the significant effect of minute changes in residence time at very high temperatures on the rate at which NO is formed.

The NO thus formed can react with more oxygen to form NO_2. Thus, the main factors in NO_x formation are: the flame temperature, the length of time the combustion gases are maintained at that temperature, and the amount of excess air present in the flame. Small combustion units operating under relatively low-temperature conditions produce an exhaust gas containing only small amounts of NO_x. The vent gas from a typical domestic gas-fired water heater, for example, contains only 10 ppm NO_x. The concentration rises rapidly with combustion intensity and may reach 500 to 1,000 ppm or more in a powerplant steam boiler.

The NO_x emissions attributed to man's activities other than combustion are relatively small, about 1 percent of total NO_x. The emissions in this category are mainly from the manufacture and use of nitric acid. In general, the NO_x concentrations arising from these sources are much greater than those of combustion sources, and they often form highly visible red-brown emissions.

Table 3-2 lists estimates of oxides of nitrogen emissions developed by the National Air Pollution Control Administration by source, using emission factors discussed in Section 8.

There appears to be little doubt that NO_2 is removed from the atmosphere by hydrolysis to become nitric acid, which is then precipitated as nitrates in rainfall or in dusts. The residence time of NO_2 in the atmosphere is only a few days.[3] NO_x is an essential part of the natural nitrogen cycle of organic growth, decomposition into the atmosphere and return to the soil as a natural fertilizer. The natural cycle is estimated to produce a worldwide NO_2 emission of about 500×10^6

Table 3–1. TIME FOR NO FORMATION IN A GAS CONTAINING 75 PERCENT NITROGEN AND 3 PERCENT OXYGEN[1]

Temperature, °F	Time to form 500-ppm NO, sec	NO concentrations at equilibrium, ppm
2,400	1,370	550
2,800	16.2	1,380
3,200	1.10	2,600
3,600	0.117	4,150

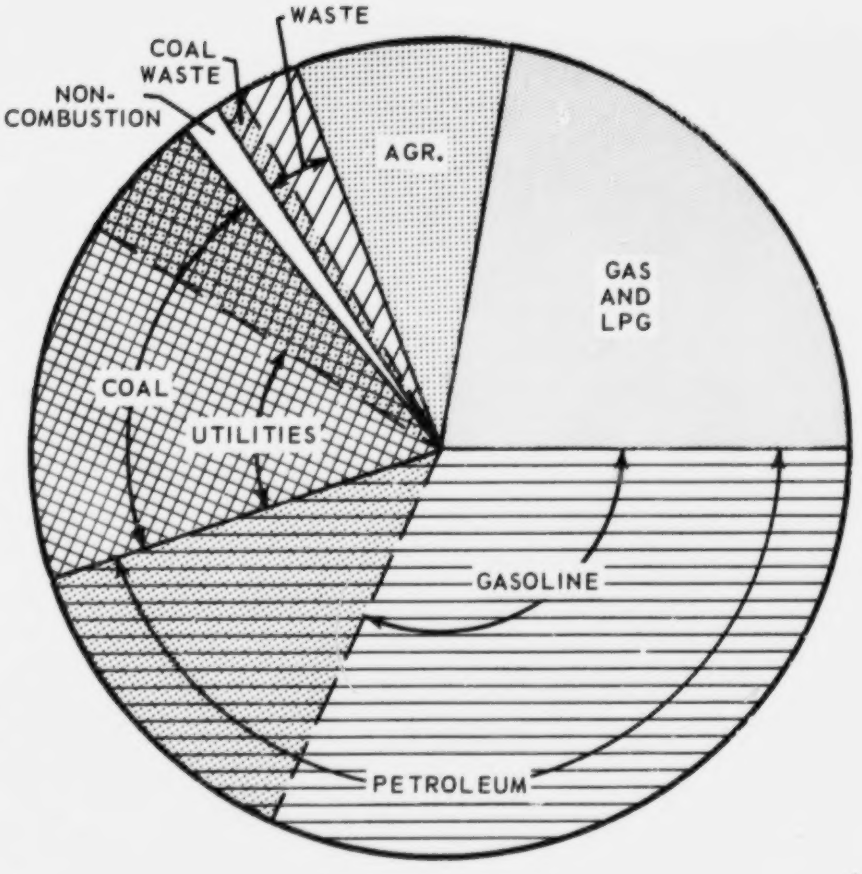
Table 3–2. ESTIMATES OF NITROGEN OXIDE EMISSIONS IN THE UNITED STATES, BY SOURCE, 1968[2]
(tons/year)

Source	Emissions
Mobile fuel combustion	
Motor vehicles	
Gasoline	6,600,000
Diesel	600,000
Aircraft	40,000
Railroad	400,000
Vessels	300,000
Non-highway users	300,000
Stationary fuel combustion	
Coal	4,000,000
Fuel oil	1,110,000
Natural gas	4,640,000
Wood	230,000
Solid waste	
Open burning	450,000
Conical incinerators	18,000
Municipal incinerators	19,000
On-site incinerators	69,000
Coal waste banks	190,000
Forest burning	1,200,000
Agricultural burning	280,000
Structural fires	23,000
Industrial processed	200,000
Total	20,669,000

tons per year.[4] Air pollution by NO_X emissions tends to become progressively worse as population becomes more dense and demands for industrial combustion energy increase.[5] The concentration of NO_X in urban areas of the United States averages 40 to 50 parts per billion (ppb),[6] which is strikingly greater than the natural background level of 1 ppb; it is this difference that creates the need for control.

Figure 3-1 shows the total amount of manmade NO_X generated in the United States in 1968, according to the type of fuel used. Both mobile and stationary sources are summarized for the sake of completeness and comparison. Emissions from mobile sources are treated at length in another document, AP-66, *Control Techniques for Carbon Monoxide, Nitrogen Oxide, and Hydrocarbon Emissions from Mobile Sources.*

Figure 3-2 presents graphically a 1968 estimate of NO_X emissions from stationary installations in the United States by types of fuel use, as developed by an independent source. After electric power plants and automobiles, the largest NO_X source is the natural-gas-driven compressor for oil and gas pipelines and gas plants. This is largely a nonurban source, which is discussed in detail in Section 7.3. A comparison between coal, oil, and gas for ordinary use in power plants or boilers is given in Table 3-3. Average emission factors on a uniform Btu basis are given. In individual units, wide variations from these data are to be expected, as discussed in Section 8 of this report. Coal, with its large emission factors, accounts for some 39 percent of all NO_X from stationary installations in the United States, or 18 percent of the total NO_X emissions shown in Table 3-2.



NO_x ESTIMATED TONS, 1968	FUEL TYPE
4,640,000	GAS AND LPG
9,350,000	PETROLEUM
6,600,000	AUTO/GASOLINE
4,000,000	COAL
2,970,000	COAL UTILITIES
746,000	WASTE BURNING
190,000	COAL WASTES
200,000	INDUSTRIAL NON-COMBUSTION
1,733,000	AGRICULTURAL, WOOD, AND FOREST FIRES
20,669,000	U. S. TOTAL

Figure 3-1. Total estimated oxides of nitrogen emissions from mobile and stationary sources in United States (20,669,000 tons), by fuel type and tonnage, 1968.

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4. COMBUSTION CONTROL TECHNIQUES

4.1 COMBUSTION MODIFICATIONS

The combustion of fossil fuels with air as the oxidant results in the formation of oxides of nitrogen. These species are formed by the direct combination of molecular nitrogen and oxygen in flames. Thus, in the combustion of natural gas, which is virtually free of bound nitrogen, the quantities of NO_x produced (in excess of 1,000 ppm NO_x in flue gases from some electric utility boilers) clearly indicate that high-temperature fixation of atmospheric nitrogen occurs. In contrast, the formation of sulfur oxide pollutants is solely dependent on the sulfur content of the fuel.

Chemically bound nitrogen in the fuel can also contribute to the overall NO_x emission from combustion processes, since it reacts with oxygen much more readily than the molecular nitrogen supplied with the combustion air.[1] These differences in reaction rates are due to the extremely stable nature of molecular nitrogen. For molecular nitrogen to react, enough energy must be furnished to dissociate the N-N bond. The bond dissociation energy is 225,000 calories per gram-mol of nitrogen, a very high value.

By contrast, the dissociation energies of the carbon-nitrogen bonds in fuel molecules fall in the more modest range of about 60,000 to 150,000 calories per gram-mol. Correspondingly, the activation energy required for oxygen to react with bound nitrogen in the fuel is substantially lower than that required for reacting with molecular nitrogen. Except at very high temperatures, therefore, NO_x is formed at a higher rate via the oxidation of fuel nitrogen than through the reaction of oxygen with molecular nitrogen. The formation of NO_x from nitrogen in the fuel may be relatively unaffected by changes in combustion conditions, according to the limited data available.[1,2,3] This problem requires more research, particularly on coal combustion.

The role of the fuel nitrogen content in combustion at the usual boiler temperature has been studied in laboratory experiments, which indicate NO_x is formed by the oxidation of fuel nitrogen.[1] Elshout and Van Duren[2] also correlated data on NO_x in fuel oil combustion and found a trend toward an increase in NO_x emissions with increasing fuel nitrogen content. These correlations may be treated as tentative, however, since other boiler operating variables were not considered.

Recent data, obtained by Argonne National Laboratories, from tests in which oxygen-argon replaced air, showed that oxides of nitrogen can be formed in low temperature combustions exclusively via the oxidation of fuel nitrogen. Combustion of a fluidized bed of coal was run with 20 percent oxygen in nitrogen and with 20 percent oxygen in argon. The amount of NO produced was essentially the same in both cases and was about the same as that obtained with a conventionally fired package boiler.[3]

In high-temperature combustion processes, the elementary reactions between atmospheric nitrogen and oxygen clearly play a dominant role in NO_x formation. Under typical combustion conditions, the only oxide of nitrogen of any consequence is nitric oxide. Thermodynamic equilibrium highly favors the formation of NO over that of NO_2 at high temperatures (as shown in Table 4-1). Once formed at high temperatures, the NO can react with excess oxygen to yield NO_2. Although this oxidation reaction has a negative temperature coefficient, i.e., its rate decreases with increasing temperatures, the residence time usually available in combustion equipment is too short for an appreciable

Table 4–1. CALCULATED EQUILIBRIUM CONCENTRATION OF NITROGEN OXIDES[a] (ppm)

Temperature, °F	Air		Flue gas[b]	
	NO	NO_2	NO	NO_2
80	3.4×10^{-10}	2.1×10^{-4}	1.1×10^{-10}	3.3×10^{-5}
980	2.3	0.71	0.77	0.11
2,060	800	5.6	250	0.87
2,912	6,100	12	2,000	1.8

[a] For the reactions: $N_2 + O_2 \rightleftarrows 2\,NO$

$2NO + O_2 \rightleftarrows 2\,NO_2$

[b] 3.3% O_2, 76% N_2 in flue gas.

fraction (more than 5-10%) of the NO to be oxidized to NO_2. The bulk of the NO_2, favored by the thermodynamic equilibrium under ambient conditions, is produced in the atmosphere, rather than within the confines of the combustion source.

The rate of NO formation is very highly temperature dependent, and as a result, Zeldovich estimated an activation energy of 129 Kcal/mole for this reaction.[4] He gives the following expression for the rate of formation of NO, derived on the basis of the chain mechanism of reactions:

$$\frac{d(NO)}{dt} = 3.0 \times 10^{14} e^{-129{,}000/RT} (N_2)(O_2)^{1/2}$$

Where:

(NO), (N_2), and O_2 = Concentrations, gram-mols/cm^3

t = Time, seconds

T = Temperature, °Kelvin

R = Gas constant, cal/gram-mol/°K.

More recent data verify this magnitude of the activation energy.[5]

The very high activation energy for NO formation accounts for the extreme dependence of reaction rate on temperature. The gas-phase decomposition of NO back into N_2 and O_2 has a lower, but still appreciable, activation energy. This means that NO, once formed, is extremely stable; that is why it is difficult to remove it from a gas in trace amounts.

Catalysts may speed up both the formation and decomposition.

A number of investigators have studied the NO decomposition reaction, and various estimates have been made for the kinetic parameters of this process.[5-8] It appears that below 1100°K, NO decomposition is catalyzed by surfaces, while above 1400°K it is strictly a gas-phase reaction. From the standpoint of practical applications, i.e., using combustion modifications to control NO_x emissions, the most important factor in the NO chemistry of flames is the rate of formation of NO.

Since NO formation is highly temperature dependent, the reduction in NO_x emission effected by relatively modest peak flame temperature reductions can be very significant. This is, of course, an over-simplification of the actual situation, in that not only the peak flame temperature, but the entire time-temperature history of the combustion process requires control. Nevertheless, relatively simple techniques aimed at the reduction of peak flame temperatures have been successful in accomplishing reductions in NO_x emissions of the order of 50 percent, compared with "standard" operating practices.

Movement of the combustion gases through different zones of temperature, pressure, and concentrations influence the formation of NO. The principal factors affecting NO_x

production are flame temperature, the excess air present in the flame, and the length of time that the combustion gases are maintained at flame temperature. Most of the NO is formed in the flame where the highest temperatures prevail. As indicated, the level of emissions is also influenced by the amount of excess air present. The lower the excess air, the lower the NO_X emissions and vice versa. Excess air beyond a certain level dilutes the flame and, therefore, decreases the flame temperature and decreases NO_X.

When residence time of combustion gases at the high flame temperatures is relatively short, the NO reaction is prevented from reaching equilibrium. Figure 4-1 shows theoretical concentrations of NO calculated on the basis of typical fuel analyses, excess air conditions, and a residence time of 0.5 second.[9] The strong dependence of NO formation on temperature is readily apparent in Figure 4-1. At high temperatures, such as in the flame, appreciable NO is formed; but below 2,800°F, formation is negligible (see Section 3.1 above). Furthermore, the NO reaction is reversible, and some of the NO decomposes to nitrogen and oxygen. If sufficient time were available, the decomposition reaction could also proceed to equilibrium. In a boiler, industrial furnace, or engine, however, the gases move quickly from the hot flame zone to cooler regions, and the rapid decrease in temperature freezes the NO concentration at a level exceeding that corresponding to the equilibrium value at exhaust or flue gas temperature. The key to reducing NO_X emissions by modification of the combustion process, consequently, depends on some combinations of lowering peak flame temperature, altering the time-temperature profile in the furnace, and reducing oxygen and nitrogen availability for reaction.

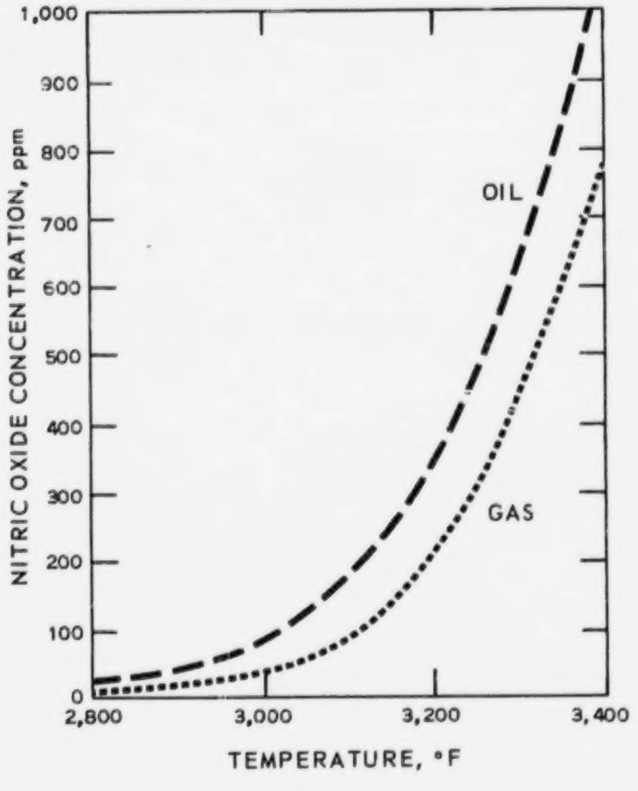

Figure 4-1. Calculated nitric oxide concentration from oil- and gas-firing, 0.5 second residence time excess air.

Because of the potential simplicity of NO_X control via combustion modification, this area is regarded as the most promising method of controlling NO_X emissions. If successfully applied, the modification of design features or operating conditions could be the least expensive and most readily applicable technique of NO_X control for various types of combustion equipment. At least partial success has been found for NO_X reduction by a number of combustion modifications, which will be discussed further.

4.1.1 Factors Affecting NO_X Emissions

Theory predicts that high or low NO_X emissions are the result of design or operating conditions on flame temperature, excess air, and residence time. Present theory is useful in explaining certain specific phenomena, but is not comprehensive enough to explain all the interactions of the many variables having an effect on the process. Experience has shown that the levels of NO_X emission in a particular combustion unit cannot be predicted based on theoretical considerations or generalized data correlations. In fact, not only do emissions vary extensively between units having similar operating conditions, but they may even be widely different in identical equipment.

4.1.1.1 Fuel Type and Composition

It has been shown that the type of fuel fired can have an effect on the quantity of NO_X emissions produced, and that these emissions vary further with the kind of equipment in which the fuel is consumed. This is illustrated in Table 3-3, wherein NO_X emissions with coal were shown as highest in all categories. Emissions from fuel oil firing are next highest, and gas firing is lowest. Recent experience in the electric generation industry in California has shown, however, that NO_X emissions with natural gas can be substantially higher than with fuel oil, particularly for large boilers (See Section 8).

As discussed in Section 4.1, the chemically bound nitrogen in the fuel (coal and oil) may also be converted into NO_X. Other fuel properties such as carbon-to-hydrogen ratio, ash and metals content, and fuel gravity and viscosity may also be important. The effect of most of these factors remains to be defined.

4.1.1.2 Heat Release and Transfer Rates

The heat release in a given furnace volume has an important bearing on the flame temperature produced. The amount of cooling surface surrounding the combustion zone not only has an effect on the flame temperature, but also affects the quench rate in the flame. The interaction between these two factors influences the NO_X emission rate. In other words, if heat release rate increases but heat transfer does not keep pace, furnace temperature increases and so does NO_X formation. The trend in the public utility industry is toward much larger boiler and turbine installations than those presently in existence. Firing rates in these units, of necessity, have increased, with resultant higher flame temperatures. The installation of a larger number of burners in these units is required to achieve the desired firing rate. The result is that the burners and the flame are spread throughout a wider portion of the furnace.

It is also well known that NO_X emissions decrease with a decrease in furnace loading, a direct result of heat release rate. Tests at full, one-half, and one-quarter load resulted in nitric oxide values of 300, 185, and 145 ppm, respectively.[10] Furthermore, it has been observed that emissions not only vary with heat release rate, but that they also vary with the fuel type in different installations at the same heat release rates. Figure 4-2, based on data reported by Sensenbaugh and Jonakin,[9] illustrates these points.

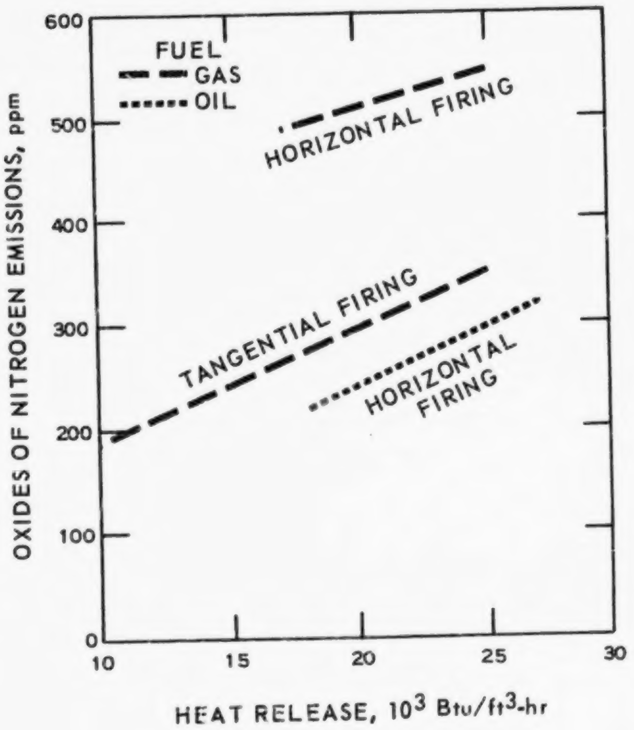

Figure 4-2. Effect of heat release on oxides of nitrogen emissions, by type of firing.

A number of investigators have noted the effects of heat release rate in a given furnace volume on NO_2 concentrations. There is little doubt that the heat release rate is an important parameter having a direct bearing on peak flame temperature. Furthermore, it has been suggested that for very large boilers, oil flames, because of higher emissivity, may have a more rapid rate of heat removal by radiation than nonluminous gas flames, so that the oil flame may give a lower effective residence time at peak temperatures.[11] The use of carburetted flames has been considered as one means to increase the emissivity of the nearly colorless flames normally obtained in the combustion of natural gas.

4.1.2 Modifications of Operating Conditions

Combustion modification techniques aimed at lowering the level of NO_x emissions can be divided into two broad categories. In the first category of these techniques, the operating conditions in fossil fuel combustion processes are modified. In the second category (to be discussed in Section 4.1.3), combustion equipment design modifications can be used to lower NO_x emissions. Some of the designs and operating conditions that decrease NO_x emissions may tend to increase emissions of CO and hydrocarbons or decrease fuel efficiency.

4.1.2.1 Low Excess Air Combustion

Low excess air combustion is one of the most promising and universally applicable methods of reducing NO_x by combustion modifications. Special control equipment and very careful supervision are required to avoid explosions, carbon monoxide, smoke, and unburned fuel emissions; these can be minimized, however, by the usual operations at excess air levels from 15 to 50 percent. This procedure consists of supplying as close to stoichiometric requirements of air for complete burnout of fuel as is permitted by the nature of the combustion process.

Low excess air combustion is a technique originally developed in the United Kingdom to overcome undesirable operating conditions such as low-temperature corrosion and air heater plugging in oil fired boilers.[12] Later, European boiler operators made further refinements in this type of operation, claiming additional operating advantages, particularly improvements in furnace slagging and heating-surface fouling. In the early 1960's, this operating technique was introduced to public utilities in the United States and subsequently adopted as a regular practice at some oil-fired power stations. While theory predicts a reduction of NO_x emissions with lower excess air, actual data are still limited on this type of operation. The investigations by Sensenbaugh and Jonakin (1960),[9] on oil-fired boilers also showed that NO_x emissions decrease as the oxygen content of the flue gas is reduced, even at the higher levels of excess air. As shown in Figure 4-3, NO_x reductions of 36 percent in a horizontal oil-fired boiler and 28 percent in a tangentially fired unit were obtained as flue gas oxygen content was decreased from 3.5 to 4.0 percent to about 2 percent. Subsequent investigations[12-14] at much lower excess air (2 to 3 percent excess air, 0.4 to 0.6 percent O_2) in oil-fired installations indicate NO_x reductions of up to 63 percent can be achieved by lowering excess air from 15 percent to about 2 to 3 percent. Figure 4-4, based on a report by Fernandez, Sensenbaugh, and Peterson,[13] illustrates the magnitude of NO_x reductions possible in oil-fired boilers operating at low excess air. Similar effects have been observed in laboratory tests of an oil-fired domestic heating installation[14] with a level of excess air much higher than that in the larger utility boilers.

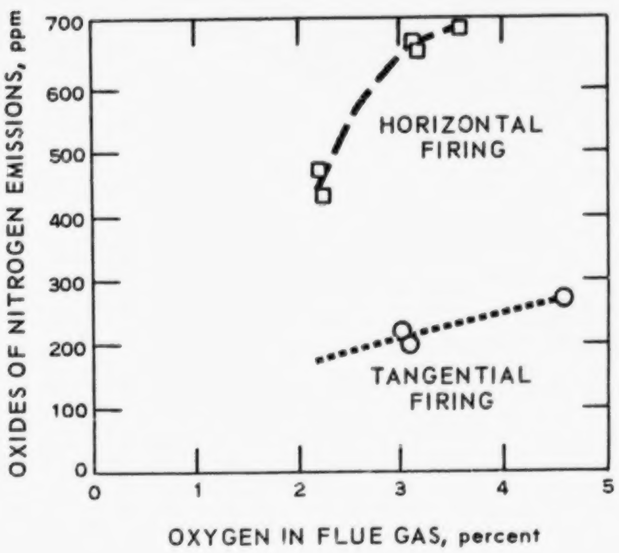

Figure 4-3. Effect of excess air on oxides of nitrogen emissions from oil-fired boilers.[9]

Laboratory data reported by Bienstock[15] indicate that with a single small burner and

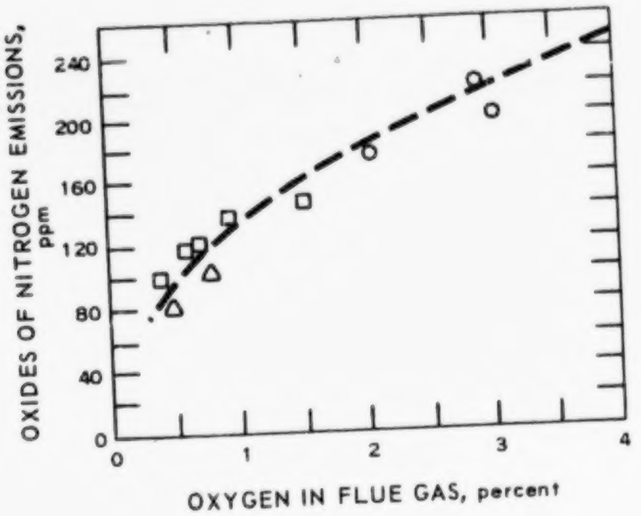

Figure 4-4. Oxides of nitrogen emissions from oil-fired boilers at low excess air.[13]

correspondingly simple controls, both low excess air and two-stage combustion do give lower values of NO_X with coal. By reducing the excess air fed to the primary combustion zone from 22 to 50 percent, a 62 percent reduction of NO_X was obtained at carbon combustion efficiencies of 98 percent. This combustion efficiency was improved to 99.2 percent by injecting an additional 17 percent of air just beyond the flame front, with the same reduction in NO_X.

There are engineering difficulties in reducing these laboratory data to practice, but in view of the importance of coal as a fossil fuel, the incentive for a successful development is great.

4.1.2.2 Flue Gas Recirculation

The use of flue gas recirculation in combustion processes is not new. This is a process in which a portion of the combustion flue gas (say 10-20% of feed to the furnace) is recirculated into the combustion zone.

Gas recirculation as practiced in utility plants for boiler tube temperature control does not fulfill the requirements of "flue gas recirculation for NO_X control," because the recirculated gases are injected downstream of the burners. The flue gas must enter directly into the combustion zone if it is to be effective in lowering the flame temperature and reducing NO_X formation.

Processes using this technique provide some means for recycling a portion of the flue gases produced back to the combustion chamber. The effect of recycling on combustion conditions depends on (1) the point of injection into the combustion system and (2) the amount of gas recycled. The greatest effect on flame conditions is achieved by mixing the gases directly with the combustion air. Injecting flue gas directly into the primary flame zone has the effect of (1) decreasing flame temperature, and (2) diluting the combustion air (oxygen) and the resultant flue gases. Where flue gas is introduced downstream of the combustion process, the effect is largely one of dilution. The quantity of gas recirculated is of major importance, having a direct effect on the combustion conditions desired.

Some large steam boilers are designed for recirculation of a portion of the flue gases in order to control superheat temperatures. Normally, as boiler load decreases, steam temperatures tend to drop off unless some method of control is employed. By recirculating an increasing portion of the flue gas as the boiler load decreases, it is possible to maintain steam temperature at a constant level over a wider load range. Where this type of control is used, the flue gases are injected to reduce the effectiveness of the furnace heat absorption surface without interfering with the combustion process. Tests made during the California joint project NO_X investigations in 1960-1962 concluded that recirculation for steam temperature control was relatively ineffective in suppressing NO_X. Recent unpublished data, however, indicate that recirculation of 20 percent of the gases in a gas-fired boiler equipped with recirculation steam temperature control reduced emissions by 20 percent.[11] It should be recognized that the objectives of recirculation for NO_X control may not be compatible with the objectives for steam temperature control.

Exhaust gas recycling has also been found to be effective in controlling NO_X in internal combustion engines. It has been shown[11,16] that an 80 to 85 percent reduction in NO_X

can be achieved in the internal combustion engine, albeit at the expense of operability. Laboratory tests of an oil-fired domestic heating furnace[13] have shown potential reductions of 70 percent when recycling 50 percent of the flue gas, as shown in Figure 4-5 The data presented in Figure 4-5 indicate that reductions in emissions up to 80 percent can be achieved by the combination of reducing excess air from 50 to 20 percent and recirculating 50 percent by volume of the flue gas. Combining low excess air combustion with flue gas recirculation has a further advantage in that it makes it easier to achieve smokeless combustion, in addition to the reduction in NO_X. Gas recirculation has also been employed in low-temperature heating furnaces in industrial applications to achieve greater and more uniform heat transfer into the product. Vertical shaft lime kilns often use recirculation to control calcining temperatures more effectively. The effect on NO_X emissions in the latter cases, however, is not known, but further investigation is warranted.

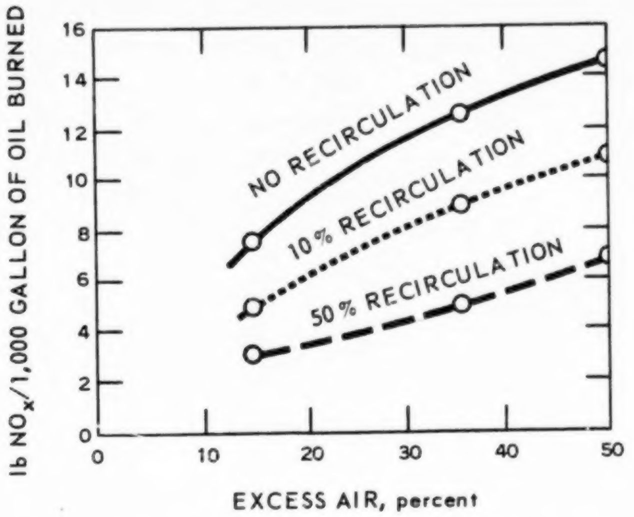

Figure 4-5. Combined effect of flue gas recirculation and excess air on oxides of nitrogen emissions from an oil-fired domestic heating furnace.[14]

The mechanism for the reduction of NO_X emissions via flue gas recirculation has been attributed to the effect of decreasing flame temperature and to dilution of the available oxygen in the flame zone.[14] Investigators at the Bureau of Mines have concluded that for gas-fired appliances this reduction in NO_X is due only to the lowering of the flame temperature and not to reactant dilution.[17] If this is true, the ability to accomplish the same end by other thermal means suggests the possibility of other solutions to the NO_X problem. Gas recirculation, regardless of its action in reducing NO_X, offers considerable potential for application to many existing installations, with the possible exception of those dependent on high flame temperature, i.e., melting furnaces. The extent of applicability of this type of combustion modification must still be investigated. The quantity of recirculated gas necessary to achieve the desired effect in different installations is important and can influence the feasibility of the applications. For instance, recirculating large quantities of gas in utility boilers poses problems in the handling of large quantities of gas, in addition to the problem of increased investment and operating costs.

4.1.2.3 Steam and Water Injection

Flame temperature, as discussed above, is one of the important parameters affecting the production of NO_X. There are a number of possible ways to decrease flame temperature via thermal means. For instance, steam or water injection, in quantities sufficient to lower flame temperature to the required extent, may offer a control solution. Water injection was found to be very effective in suppressing NO_X emissions from an internal combustion engine.[18] Water injection may be preferred over steam in many cases, due not only to its availability and lower cost, but also to its potentially greater thermal effect. In gas- or coal-fired boilers, equipped for standby oil firing with steam atomization, the atomizer offers a simple means for injection. Other installations will require special rigging so that an investigation program will be necessary to determine the degree of atomization and mixing with the flame required, the optimum point of injection, and the quantities of water or steam necessary to achieve the desired effect. The use of these techniques for NO_X control may carry with them some undesirable operating conditions, such as decreased efficiency and higher corrosion rates; and these must also be evaluated.

4.1.3 Design Modifications

4.1.3.1 Burner Configuration

The specific design and configuration of a burner has an important bearing on the amount of NO_X formed. Certain design types have been found to give greater emissions than others. For example, the spud-type gas burner appears to give a higher emission rate than the radial spud type, which, in turn, produces more NO_X than the ring type. (See Figures 4-6, 4-7).[11] Similarly, the spray angle in oil atomizers can affect NO_X; narrower spray angles, producing poorer atomization, have been reported to provide lower NO_X emissions,[11] contrary to the results of Barnhart and Diehl.[19]

Some burners, such as the cyclone and vortex types, operate under highly turbulent, high intensity conditions. In field tests of conventional utility burners,[11] adjustments made on burners to decrease turbulence to a minimum reduced NO_X emissions by 40 percent, but resulted in unsatisfactory flame conditions. Throttling the burner registers to increase windbox pressure and turbulence increased NO_X emissions by more than 15 percent. It appears in general that long "lazy" flames seem to favor lower NO_X emissions, in contrast with the short, intense flames usually considered desirable for combustion.

In the course of the California investigations in the late 1950's, a two-stage combustion type of burner was developed and is currently being used in a number of Los Angeles County power stations. In this type of burner, about 85 to 95 percent of the stoichiometric air needed for combustion is admitted to the flame through the burner throat. The remainder of the air required for complete combustion is injected through ports above the burner to complete the burnout of the initial combustion phase. When such operating conditions were used, reductions of 30 percent in NO_X emissions were observed, whereas admission of only 90 percent of the stoichiometric air into the primary zone resulted in a 47 percent reduction of NO_X.[19] This technique has been applied successfully to oil and gas firing, but the engineering problems of applying it to the coal-fired boilers have not been solved (see Section 4.1.2.1).

NO_X emissions may be explained by a combination of several factors. First, there is a lack of available oxygen for NO_X formation when the first stage is operated under substoichiometric air conditions. Second, the flame temperature is lower under these conditions than in normal combustion. Third, to the degree that heat is removed between stages, the maximum flame temperature in the second stage is lower than that for one-stage combustion. Fourth, the effective residence time available for NO_X formation at the peak temperatures reached in the second stage may be reduced.

Because of the effects observed with the use of two-stage combustion, it is worthwhile to consider the extension of this technique to multistage combustion for improved NO_X emission control. As a more remote possibility, the staged injection of the fuel instead of the air may result in a time-temperature-concentration profile favoring low NO_X emissions.

4.1.3.2 Burner Location and Spacing

Although data are scarce regarding the effect of burner spacing and location on NO_X, potentially these are important variables. The interaction between closely spaced burners, especially in the center of a multiple-burner installation, could be expected to increase flame temperature at these locations. There is a tendency toward greater NO_X emissions with tighter spacing and a decreased ability to radiate to cooling surfaces. This effect is illustrated by the higher NO_X emissions from larger boilers with greater multiples of burners and tighter spacing.

Tangential firing has been demonstrated to be a useful design, representing a change from other types of burner location and spacing.

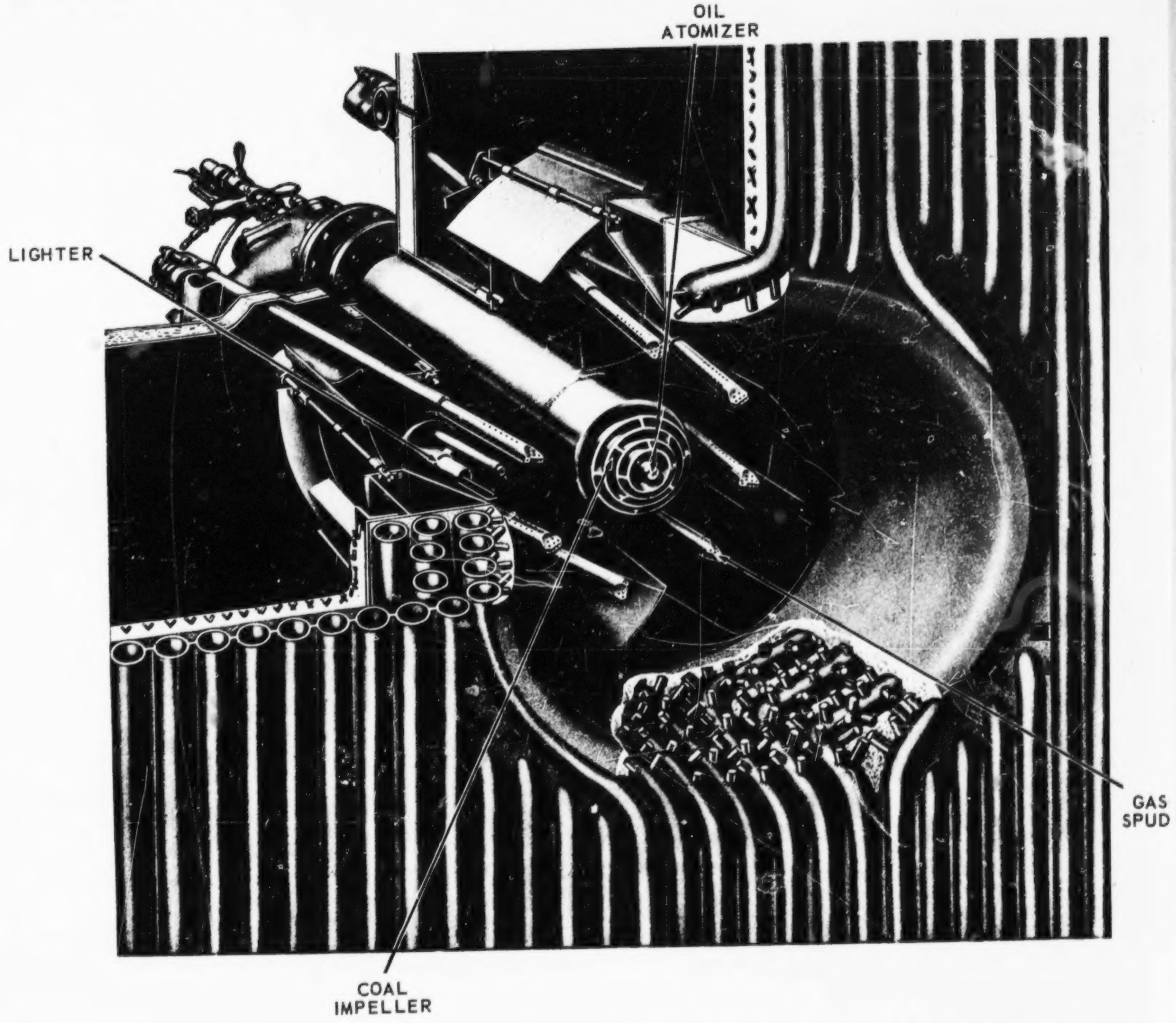

Figure 4-6. Multi-fuel burner for gas (spud-type burner), oil (circular register), and coal (circular register).

(Courtesy of The Babcock and Wilcox Company)

Burners in a tangentially fired boiler are located in the corners, firing on a tangent to a circle at the center of the furnace. As a result, individual burner flames have very little opportunity to interact with one another and the flames radiate widely to the surrounding cooling surfaces. Tangential firing can produce reductions in NO_X of up to 50 percent compared with front or opposed fired furnaces.[13] This significant effect may be exploited further for potential NO_X control in other types of combustion processes.

4.1 3.3 Fluidized Bed Combustion

Combustion of fossil fuels in fluidized beds may prove to be useful for NO_X control. Heat transfer in fluidized-bed combustion processes is excellent, so that the average bed temperature is very low (1,600° to 1,800° F) compared with conventional flame temperatures.

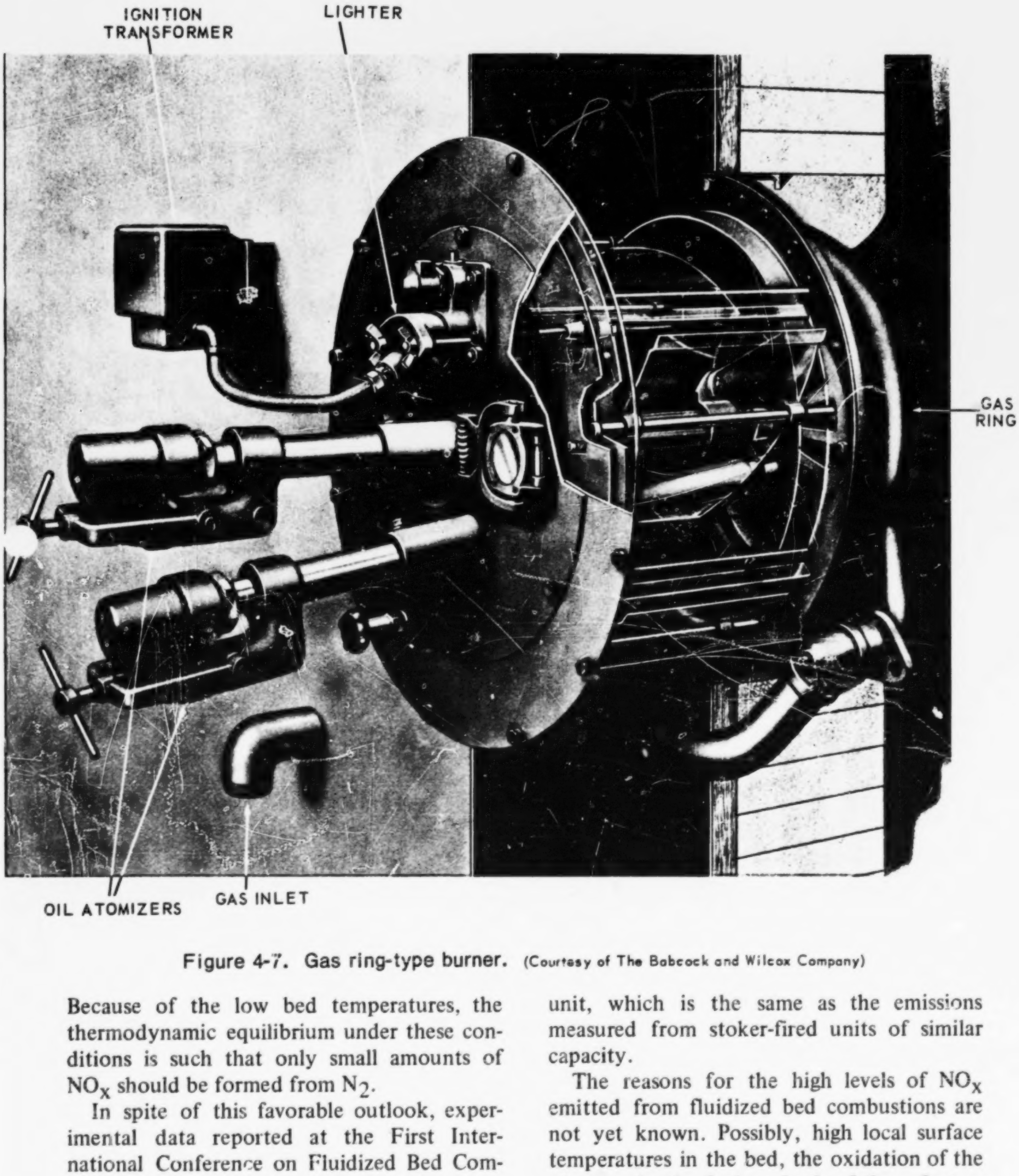

Figure 4-7. Gas ring-type burner. (Courtesy of The Babcock and Wilcox Company)

Because of the low bed temperatures, the thermodynamic equilibrium under these conditions is such that only small amounts of NO_x should be formed from N_2.

In spite of this favorable outlook, experimental data reported at the First International Conference on Fluidized Bed Combustion (Heuston Woods, Ohio, November 1968) did not show the expected reduction in NO_x emissions. For example, Pope, Evans, and Robbins measured about 0.3 pound $NO_x/10^6$ Btu fired in their coal-burning pilot unit, which is the same as the emissions measured from stoker-fired units of similar capacity.

The reasons for the high levels of NO_x emitted from fluidized bed combustions are not yet known. Possibly, high local surface temperatures in the bed, the oxidation of the nitrogen in the fuel, or both of these factors may contribute to the observed high levels of NO_x. Continuing developments of this technique may eventually result in substantial reductions of NO_x.

4.1.3.4 Small Combustion Equipment

The largest number of combustion devices in existence are installed in single-family residences. Most of these devices are small gas-fired equipment. These small sources of NO_x, such as hot water heaters and residential space-heating furnaces, are difficult to modify economically.

Premixed flames have been shown to produce lower quantities of NO_x than diffusion flames in laboratory experiments.[20,21] The application of this type of burner, eliminating or limiting the use of secondary air, may have an undeveloped potential for the economic modification of existing and new gas-fired equipment. Thus, substantial reductions in NO_x emissions from a large number of small pollution sources may be possible.

4.2 FLUE GAS CLEANING

Removing NO_x from flue gas provides an alternative means of controlling combustion-produced emissions. Such removal may ultimately become the most effective control technique in those cases where combustion modifications are not possible or are of only limited benefit. In contrast to SO_2 control, however, very little effort to date has gone into research and development of techniques for removing nitrogen oxides from flue gas. For reasons outlined more fully below, the only methods now considered practical are those that remove both SO_2 and NO_x, and the amount of NO_x removed is limited to about 20 percent or less of that found in an ordinary flue gas. The processes covered below are discussed from the standpoint of SO_2 removal in the document, AP-52, *Control Techniques for Sulfur Oxide Air Pollutants.*

A systemic study indicates that NO_x removal from flue gases will continue to be more difficult than SO_2 removal.[22] Complications arise from the fact that the nitrogen oxides present exist primarily as the stable and relatively unreactive nitric oxide, NO. Upon release to the atmosphere, the NO is oxidized slowly to the more reactive dioxide, NO_2. A second complicating factor is that the flue gases contain other reactive species such as H_2O, CO_2, and SO_2 in greater concentrations than the nitrogen oxides, and these species interfere with removal. Typical concentrations of these gases for the combustion of coal, oil, and natural gas are shown in Table 4-2. The relative reactivity of each gaseous component is suggested by the data on their solubility in water. It must be kept in mind that these solubility data are for the pure gas in equilibrium with water, each at 1 atmosphere pressure, and that the nitrogen oxides, particularly NO_2 are present in the stack gases in very low concentration. Other problems arise from the need to process very large volumes of gas for NO_x control. A modern 1,000-megawatt power plant, for example, emits about 2 million cubic feet per minute of the flue gas. Processing such a high volume of hot gas presents formidable equipment and engineering problems.

The only commercial flue gas process at present that has been reported to remove nitrogen oxides is Combustion Engineering's limewater-SO_2 scrubbing process. Other flue gas treating processes under study for SO_2 control that have shown varying abilities to remove nitrogen oxides are the Reinluft Char Process and the Tyco Laboratories' Modified Lead Chamber Process.

4.2.1 Control by Limestone Wet-Scrubbing Process

Slaked lime or limestone aqueous suspensions which are capable of removing SO_2 or SO_3 as acid gases are capable of removing a certain amount of NO_2, or NO_2 plus NO, for the same reasons. There are two basic variations of the limestone wet scrubbing process. In the first, dry limestone is injected directly into the boiler furnace where it reacts with some of the sulfur oxides (20 to 30 percent of the total SO_2, and essentially all the SO_3) ahead of a water scrubber; it is then calcined to the more reactive quicklime for use in the scrubber. In the second, limestone is added directly to the scrubber. Although

Table 4-2. TYPICAL COMPOSITIONS AND SOLUBILITY OF STACK GASES

Component	Volume percent from combustor			Solubility in water, V/V, at 1 atm, 25°C
	Coal[a]	Oil[b]	Gas[c]	
N_2	76.2	77.0	72.3	0.0018
CO_2	14.2	12.0	9.1	0.1449
H_2O	6.0	8.0	16.8	
O_2	3.3	3.0	1.8	0.0039
SO_2	0.2	0.15	--	9.41
NO_x	← 0.07[d] →			
NO (% in NO_x)	← 90-95 →			0.0056
NO_2 (% in NO_x)	← 5-10 →			Decomposes[e]

[a] Calculated for burning with 20% excess air a typical high volatile bituminous coal of the following composition: carbon, 70.1%; oxygen, 6.6%; hydrogen, 4.9%; nitrogen, 1.4%; sulfur, 3.0%; ash, 12.7%; H_2O, 1.3%.

[b] Calculated for burning with 20% excess air a typical residual fuel oil of the following composition: 86.5% C, 10.3% H, 2.5% S, 0.7% N.

[c] Calculated for burning natural gas with 10% excess air.

[d] This is an average value. Actual values range from 0.02 to 0.15%.

[e] Phase diagram in a sealed tube shows equilibrium with water a 25°C, as about 54 wt % N_2O_4 (or 120 g/100 g of H_2O).[23]

limestone in the scrubber is less efficient than lime, the second method avoids such potential boiler problems as abnormal slagging, increased erosion, and interference with combustion and temperature control. In both cases, the solids from a reactive slurry, which combines with most of the sulfur oxides and some of the nitrogen oxides. Reacted slurry, along with fly ash, is removed from the scrubber for disposal.

One disadvantage is that scrubbing with the water slurry cools the gases to the saturation temperature of about 125°F. This produces a visible and less buoyant plume; decreased buoyancy reduces the plume rise and gives higher ground-level concentrations.

The early work with limestone and lime scrubbing, done in England in the 1930's, was carried out with direct addition of the reactant to the scrubber. James Howden & Co., Ltd., and Imperial Chemical Industries, Ltd., installed lime and chalk scrubbing processes at the Fulham power plant in London and the Tir John power plant in Swansea. In pilot plant studies, Howden and ICI report[24] obtaining 60 to 70 percent removal of nitrogen oxides and 97 to 99 percent removal of sulfur oxides. These data are not typical of later results, and they may have been complicated by difficulties in the analysis for NO_x.

In the United States, UOP studied wet limestone and dolomite scrubbing at Wisconsin Electric's Oak Creek power plant. Their data[25] indicate about 20 percent removal of nitrogen oxides. Combustion Engineering studied dry limestone injection into the Boiler with wet scrubbing at Detroit Edison's St. Clair power plant.[26] Nitrogen oxide removal in this study also averaged about 20 percent. The close agreement in results obtained by UOP and Combustion Engineering and the large disparity between these results and those of Howden-ICI make the earlier data suspect.

Combustion Engineering has been offering its process (Figure 4-8) commercially. This process has already been installed by Union Electric Co. at its Meramec plant, and it is being installed by Kansas Power and Light (KP&L) at its Lawrence plant. In both cases, the boilers being outfitted are rated at 125

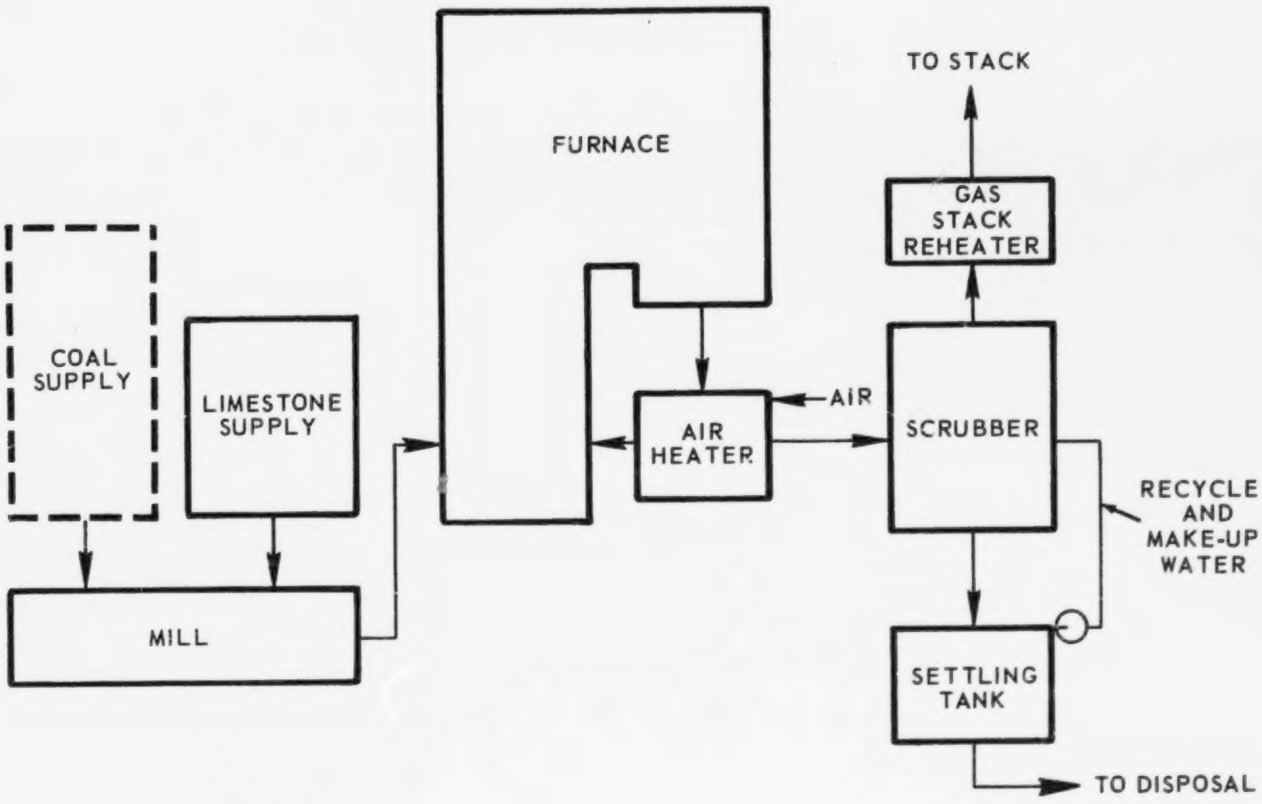

Figure 4-8. Limestone injection wet-scrubbing process.

megawatts. A number of troubles have been encountered with the Meramec plant unit.[27] This particular unit has not yet been studied with respect to NO_X removal, however.

4.2.2 Potential Control Processes

Several processes for flue gas treatment now in the research stage have shown potential for NO_X removal and are still to be developed.

4.2.2.1 Reinluft Char Process

The Reinluft Char Process uses a slowly moving bed of activated char to remove primarily the sulfur oxides from flue gases. Some NO_X may simultaneously be removed.

This process is described in Section 4.5.6 of NAPCA publication AP-52, *Control Techniques for Sulfur Oxide Air Pollutants.*

4.2.2.2 Control by Tyco Laboratories' Modified Lead Chamber Process

The flue gas treating process being researched by Tyco Laboratories, Inc., under contract to NAPCA, utilizes the chemistry of the chamber sulfuric acid process to remove both sulfur and nitrogen oxides. The basic features of the process are shown in Figure 4-9. Concentrated sulfuric acid is used to absorb both the sulfuric acid mist and the mixture of NO and NO_2 produced by recycling NO_2 into the flue gas. The acid is heated and stripped of its nitrogen oxides, which are partially converted to nitric acid; the remaining nitrogen oxides are then oxidized for recycle to the flue gas. The stripped sulfuric acid, diluted by moisture from the flue gas, is concentrated in an evaporator for recycle to the absorber with the excess constituting a second acid product.

Process consideration requires that high NO_X scrubbing efficiencies in excess of 90 percent be obtained for the process to be in NO_X balance, since about ten times as much NO_X is recycled to the system as is in the original flue gas. Thus, if a target level of 90 percent removal of the original flue gas nitrogen oxides is set, scrubber efficiencies of 99 percent are required. A second problem is

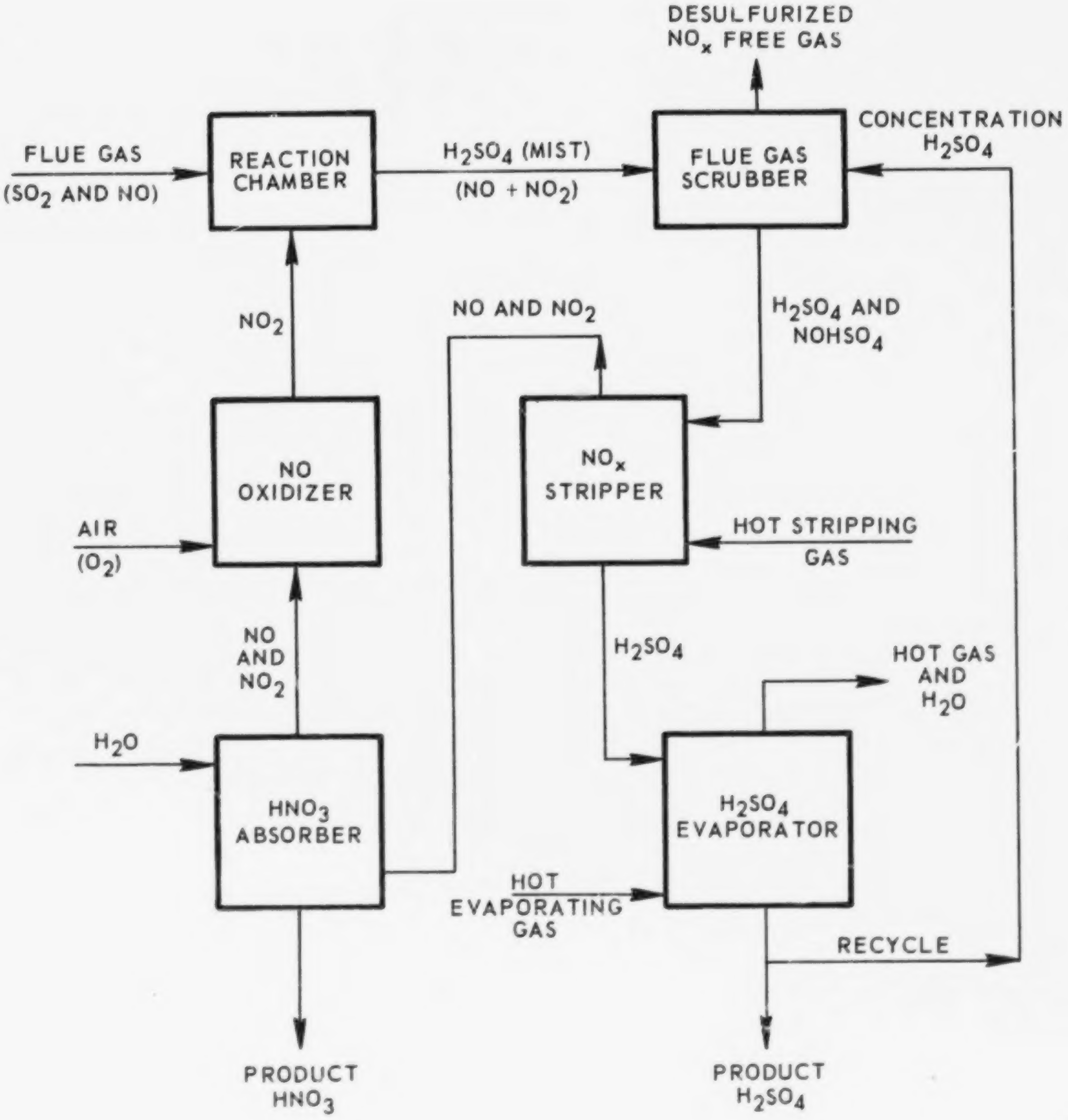
DESULFURIZED
NO_x FREE GAS
FLUE GAS
(SO_2 AND NO)
REACTION CHAMBER
H_2SO_4 (MIST)
($NO + NO_2$)
FLUE GAS SCRUBBER
CONCENTRATION
H_2SO_4
NO_2
NO AND NO_2
H_2SO_4 AND
$NOHSO_4$
NO OXIDIZER
NO_x STRIPPER
AIR
(O_2)
HOT STRIPPING
GAS
NO
AND
NO_2
H_2SO_4
HOT GAS
AND
H_2O
H_2O
HNO_3 ABSORBER
H_2SO_4 EVAPORATOR
HOT
EVAPORATING
GAS
RECYCLE
PRODUCT
HNO_3
PRODUCT
H_2SO_4

Figure 4-9. Flow diagram for Tyco process.

the very large heat load required to reconcentrate the acid diluted by the water vapor in the flue gas and to strip the nitrogen oxides. This heat load amounts to as much as 40 percent of the total heat load of the boiler. This would not be an easy requirement to meet; recent developments suggest, however, that this excessive heat load can be greatly reduced.

The flue gas treating process is still in the early stages of development, and Tyco Laboratories, Inc., is currently investigating process modifications that could reduce processing costs. Some of the modifications that have shown promise of success entail a change in the chemistry of the process whereby the NO oxidizer and the NO_X stripper are combined.

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5. LARGE FOSSIL FUEL COMBUSTION PROCESSES

5.1 ELECTRIC POWER PLANT BOILERS

5.1.1 Emissions

The largest single source of nitrogen oxide pollutants from stationary sources is boilers fired with fossil fuels. Differences between individual units may and frequently do have a major effect on the production of pollutants, especially nitrogen oxides since their emission is largely determined by the design and operation of the equipment used. For example, the type of firing, and spacing and location of burners, particularly in the large boiler units, can have a marked effect on nitrogen oxide emissions, as discussed in Section 4.1.

The total amount of NO_X emitted in 1968 by the electric utility industry for industrial and commercial purposes is given in Figure 3-2.[1]

5.1.2 Control techniques

5.1.2.1 Conversion to Lower NO_X Producing Fuel

If NO_X emissions are high with coal, intermediate with oil, and low with natural gas, on an equivalent Btu basis, substitution of the energy source by conversion to one of the lower NO_X producing fuels offers one means of reducing total NO_X emissions from a given piece of equipment. For instance, converting an ordinary boiler designed for coal- and oil-firing to the burning of natural gas could result in a reduction in NO_X emissions. The extent of the possible reduction is, of course, dependent on whether the boiler can be converted to the lower NO_X producing fuel, the design of the unit, the type of burners, the method of firing, and the differences in emission factors between the two fuels. In general, the substitution of either gas or oil for coal is expected to give a significant reduction in NO_X (Table 3-3). Emission results for oil and gas are more comparable; data available indicate that emissions from very large units can actually be greater for gas- than for oil-firing.

Although fuel type can be important in reducing NO_X emissions, the techniques used in making a conversion are of equal importance; other changes made at the same time may easily result in higher emissions. Conversion offers an opportunity for a complete revamping of the combustion system to one of lower polluting tendencies. To minimize NO_X, care should be taken in selecting the proper location, spacing, and design of burners, to assure as low a heat release as possible, to minimize flame temperature, and to provide for minimum excess air operation. Provisions for recirculating a portion of the flue gases back to the flame zone should also be considered. In addition, differences in the emissivities of the fuel types should be evaluated so that full advantage of lower NO_X producing tendencies may be realized.

There are indications that chemically bound nitrogen in fuel may play an important part in NO_X emissions (Section 4.1.1.1). If so, burning fuel with the lowest nitrogen content could reduce NO_X emission levels. For instance, it has been noted that switching to a paraffinic, "low sulfur" fuel oil of low nitrogen content in public utility boilers resulted in nitrogen oxide emissions approximately 50 percent less than those obtained when a "high sulfur" fuel oil of relatively high nitrogen content was burned.[1]

Fuel availability and price structure in the United States are complex. There are many factors involved in determining ultimate availability and price. In any given location, fuel prices and availability vary widely and are dependent upon geographical location, user category, quantity to be used, etc. While conversion to a lower NO_X producing fuel potentially offers some assistance for the NO_X problem, widespread substitutions undoubtedly would have an adverse effect on the entire fuel supply structure; ultimately, the availability, of fuel for this purpose would be limited. The subject of fuel availability, price structure, and conversion is discussed in some detail in Section 4 of AP-52, *Control Techniques for Sulfur Oxide Air Pollutants.*

5.1.2.2 Fuel Additives

For purposes of this document, a fuel additive is a substance added to any fuel to inhibit formation of NO_x when the fuel is burned. The additive can be liquid, solid, or gas; for liquid fuels, the additive should preferably be a liquid soluble in all proportions in the fuel, and it should be effective in very small concentrations. The additive should not in itself create an air pollution hazard nor be otherwise deleterious to equipment and surroundings.

As far as is known, no fuel additive is available as yet to inhibit the formation of NO_x in combustion systems. The possibility exists, however, that such an additive may be developed in the future, and it is believed that an additive of this type needs only to be capable of partially reducing NO_x formation to be useful.

5.1.2.3 Combustion Controls

Combustion modifications as potential NO_x control techniques for stationary sources of emissions were discussed in Section 4.1. These techniques have been investigated and developed in numerous laboratory test installations and in a limited number of successful applications in commercial public utility boilers.

Sufficient knowledge now exists to have reasonable confidence in the potential of these techniques for the abatement of NO_x emissions in much of the existing combustion equipment. Most of the field test work has been done on boilers, especially some of the larger sized units in public utility power plants. There is good reason to be confident of the success of such modifications to this type of equipment. In smaller units, unforeseen problems, resulting from size or operating requirements, may limit the amount of NO_x reduction.

Extensive trials of these control techniques will be necessary in many different installations in a range of sizes to determine their effectiveness and identify limitations. It is reasonable to assume that NO_x reductions of at least 20 to 30 percent using coal and perhaps as high as 60 to 90 percent using oil and gas can be achieved in much of the existing combustion equipment. It is obvious that not all of the proposed control techniques will be applicable to every process, but it is entirely possible that in most cases, one or a combination of methods may be found to be effective in achieving reasonable control.

Low-excess-air combustion, flue gas recirculation, two-stage combustion, water or steam injection, and possible combinations of these methods appear to be the most promising potential control techniques (Section 4.1.1). In large power-generation-station boilers, fired by gas and oil,[2-4] applications have shown that low-excess-air operation may reduce NO_x emissions by 30 to 60 percent, the range of reduction depending on the lowest level of excess air achieved, design of the boiler, and the type of firing.

Similarly, flue gas recirculation has proved to be effective in suppressing NO_x emission from these installations. In a utility boiler, reductions of about 20 percent have been reported when the flue gas was reinjected through ports in the bottom of the furnace. In a test installation using domestic heating oil, reduction of NO_x emissions by 50 to 65 percent was achieved by mixing recirculated flue gas with the combustion air before combustion.[5] Two-stage combustion was found to be successful in reducing NO_x by 30 to 47 percent in utility boilers in cooperative investigations conducted in southern California by the Babcock & Wilcox Company and Southern California Edison Company.[6] Tangential firing, as opposed to front wall or opposed firing, was also found to produce from 30 to 40 percent less NO_x.[2,7] The combination of reducing excess air and eliminating firing in the top eight burners in two 750-megawatt boilers at the Pacific Gas and Electric Company's Moss Landing Power Station successfully reduced NO_x by about 90 percent, from 1,500 ppm down to an average of 175 ppm.[8] Substoichiometric air was supplied to the bottom of 40 burners and the top 8 burners were used as ports to supply air for complete burnout.

Steam or water injection as a method of control has not as yet been demonstrated as an effective control technique. The quantities of steam or water required to obtain a large reduction in NO_x may make this application unrealistic and uneconomical, but the use of moderate quantities of steam or water to trim peak temperatures, when used with other combustion control modifications, may prove reasonable and helpful.

5.1.3 Costs

Estimated costs of control of NO_x emissions by a new 1,000-megawatt utility power plant are shown in Table 5-1. Approximately the same figures will apply to the modification of an existing plant using low excess air

Table 5-1. ESTIMATED CONTROL COSTS AND REDUCTION OF NO_x EMISSIONS, FOR A 1,000-MEGAWATT BOILER USED 6,120 HOURS/YEAR BY SELECTED METHODS AND BY TON

Control method	NO_x reduction, %	Fuel used	Control cost/yr, $	NO_x reduction, tons/yr	NO_x control costs, $/ton
Uncontrolled (base case)	0	Gas	0	53,000[a]	0
	0	Oil	0	30,000[a]	0
	0	Coal	0	30,000[a]	0
Low excess air	33	Gas	- 95,000[b]	17,500	- 5[b]
	33	Oil	-297,000[b]	9,900	-30[b]
	25	Coal	- 79,000[b]	7,500	-11[b]
Two-stage combustion	50	Gas	0	26,500	0
	40	Oil	0	12,000	0
	35	Coal	299	10,500	29
Low excess air plus two-stage combustion	90	Gas	- 95,000[b]	47,700	- 2[b]
	73	Oil	-297,000[b]	21,900	-14[b]
	60	Coal	220,000	18,000	12
Flue gas recirculation	33	Gas	202,000	17,500	12
	33	Oil	202,000	9,900	20
	33	Coal	202,000	9,900	20
Low excess air plus flue gas recirculation	80	Gas	107,000	42,400	3
	70	Oil	- 95,000[b]	21,000	- 5[b]
	55	Coal	123,000	16,500	3
Water injection	10	Gas	144,000	5,300	27
	10	Oil	179,000	3,000	60
	10	Coal	143,000	3,000	48

[a] Uncontrolled method, total NO_x emitted; no reduction.

[b] In instances wherein the installation of control equipment results in a savings, control costs are listed as negative numbers.

and/or two-stage combustion, excluding the costs of downtime and assuming that space and facilities are available. NO_X reduction using low excess air shows a net return, for a large plant where the necessary control equipment and operators are already available.

5.1.3.1 Limitations with Large Coal-Fired Boilers

Low-excess-air operation and two-stage combustion have not yet been found feasible for application in large pulverized coal-fired boilers. There are serious engineering difficulties to be overcome in this type of operation, despite the fact that small-scale laboratory experiments indicate the technology might be useful, if it could be made to work (Section 4.1.2.1). Achieving low-excess-air operation is dependent on obtaining a reasonable uniformity of air/fuel ratios in all burners, to avoid unburned fuel, increased carbon monoxide and hydrocarbon in flue gas, and reduced safety of operation. With pulverized coal, this is difficult because of the imbalances between primary air and coal streams in individual burners, and the further imbalance created by mixing these streams with secondary air at the burner. Use of low excess air tends to increase the production of CO and hydrocarbons. Decreasing excess air increases flame temperature in the furnace, which can promote slagging and corrosion of furnace tubes; but a small amount of steam or water injection could possibly be used to control the problem of flame temperature.

Two-stage combustion has not been applied in pulverized coal-firing as yet. This modification delays the combustion process, however, and its appplication to pulverized coal may increase unburned fuel losses to a point where efficiency is impaired and the process becomes uneconomical.

The effectiveness and applicability of NO_X control through combustion modifications to industrial and commercial boilers will, in general, follow the same pattern as discussed above for public utility power plant boilers, especially when these units are large and comparable in design and configuration to the electric utility boilers. Since commercial and industrial boilers are normally smaller in size, however, the cost of installing potential controls on a unit basis could be expected to be higher. When these boilers are fired by pulverized coal, application of the techniques may also be limited, as, for example, in the case of utility units. There is reasonable assurance, however, that the suggested controls can be effective in gas- or oil-fired boilers of this category.

5.1.3.2 Packaged Boilers

The majority of packaged water-tube or fire-tube boilers are fired with natural gas or oil. Those fired with coal are usually stoker-or grate-fired. For physical reasons, packaged fire-tube boilers have a maximum rating of about 25,000 pounds of steam per hour; while water-tube packaged boilers of a capacity as great as 250,000 pounds/hour are now being sold. In general, the larger the installation, the easier it is to justify installation of combustion modification control equipment. Modifications to control NO_X can, however, complicate the automatic controls required for reliable operation. For the gas- and oil-fired packaged boiler, modifications may not be as difficult as they are for coal-fired installations. Low-excess-air firing with oil- and gas-fired packaged boilers might be relatively easy to achieve and have the potential of reducing NO_X by 30 to 50 percent.

For low-excess-air firing, burners will have to be redesigned and additional instrumentation supplied to provide closer control of the air/fuel ratio in correspondence with load modulation. Burner redesign may be relatively simple and inexpensive; only minor modifications to the existing burners may be required to achieve the level of excess air desired. The costs of these modifications, however, will be dependent on the number of burners, the size of the equipment, and the necessary changes in the control system. These costs will be partially or completely offset by increased efficiency and decreased maintenance and operating costs. An increase of from 1 to 2 percent in efficiency may result, and the corresponding fuel savings will help to defray alteration costs.

Many packaged boilers are designed for pressure firing, with the forced draft fan mounted as a part of the burner. When flue gas recirculation is considered for NO_X control, the position of the forced draft fan may complicate the installation of necessary modifications. Some means must be provided for taking gas near the boiler exit and injecting it into the air stream so that it mixes with the combustion air. Normally, this will require a separate fan and additional duct work. Space is a limiting factor in packaged boilers, and should be taken into consideration when flue gas is to be recirculated. Recirculation can reduce NO_X emissions in packaged boiler installations potentially by 30 to 40 percent; if combined with low-excess-air firing, reductions up to 60 to 70 percent may be achieved. Recirculation may also make it possible to achieve lower-excess-air operation without smoke. Specific costs for conversion of a packaged boiler designed for pressure-firing to flue gas recirculation will be highly dependent on the amount of gas to be recirculated (fan), ductwork required, the size of the unit, and the controls already available.

Two-stage combustion has not been used with packaged boilers and may be difficult to install except on larger units. An exception might be the stoker- or grate-fired units, where overfire air may create the necessary turbulence to improve combustion. In some packaged boilers, compact size and small combustion space will make two-stage combustion impractical. Two-stage combustion delays the combustion process by accomplishing the initial combustion phase under substoichiometric conditions and completing burnout downstream with air injected through overfire air ports. In many instances, the combustion zone is too small for this technique so the potential effectiveness has to be evaluated for each specific design. When it can be applied, two-stage combustion could achieve the same order of NO_X reductions (30 to 40 percent) in smaller packaged boilers as in the larger units, but costs increase as sizes decrease.

5.2 STATIONARY ENGINES

As has been pointed out in previous discussions, the combustion of fuels with air forms oxides of nitrogen by the direct combination of molecular nitrogen and oxygen in the flames. The thermodynamics and kinetics of the reaction indicate that control of NO formation must be accomplished by lowering flame temperatures, limiting the availability of the reactants (oxygen and nitrogen), or controlling net reaction rates. These principles apply to combustion inside engines as well as in a less confined space such as in a furnace.

The stationary engine population of the United States includes both reciprocating piston engines and gas turbines. The United States reciprocating piston engine population is distributed[9] as given in Table 5-2.

5.2.1 Piston Engines

No information on the power capabilities of the total United States installed piston engine population has been located. From distillate fuel oil consumption in "industrial and

Table 5-2. STATIONARY RECIPROCATING PISTON ENGINES IN UNITED STATES, 1967

Engine type	Fuel	Percent of Total[a]
Full diesel	Liquid fuel oil	15
Dual fuel	Liquid or gas	19
Spark-ignition gas	Gas	66

[a] It is estimated 85 percent of these engines are supercharged;[10] about 1 percent are the precombustion-chamber type.[9]

other" stationary engine applications,[11] however, it is estimated that the total current piston engine capacity may approximate 70 million hp, assuming that two-thirds engines are gas-fired, and using service time factors of 0.6 for prime movers in manufacturing installations, 0.2 in electric utility uses, and a fuel consumption of 0.4 pound fuel/brake hp-hour. This estimation is probably low because some large oil-fueled diesel engines undoubtedly use heavy fuel oil, which would not appear in the distillate fuel figures. Estimates of total United States NO_x produced by stationary engines are given in Table 5-3.

5.2.1.1 *Emissions*

The NO_x emission characteristics of various types of piston engines are listed in Table 5-3. It should be emphasized that these data are based on experiments using relatively small engines, such as 200-hp truck engines, and there may be some question about extrapolating the data to larger engines. It is believed, however, the data do provide a valid indication of the effect of various engine variables. Data on the gas turbine engine are from conventional aircraft turbojets. Some preliminary and tentative observations can be made:

1. Turbocharging a piston engine may increase NO production.
2. A precombustion-chamber piston engine seems to produce about one-third as much NO_x as a direct-injection, piston engine.
3. An oil-fired turbojet engine may produce about 0.1 as much NO_x as an oil-fired, direct-injection diesel engine.

Table 5-4 summarizes data obtained in tests on two large dual-fuel (oil and gas) stationary diesel engines. The larger engine operated at a lower brake mean effective pressure (BMEP) and engine speed than the smaller engine. The air/fuel ratio was higher than those normally found in automotive diesels under similar load conditions, and extremely low particulate emissions were observed. The data suggest that slower engines produce higher concentrations of NO_x; this is to be expected for the longer residence time of the gases at high temperatures in the engine cylinders.

5.2.1.2 *Control Techniques*

These observations, together with other general background knowledge, suggest that the following techniques to control NO_x

Table 5-3. ESTIMATED STATIONARY ENGINE DISTRIBUTION IN UNITED STATES, 1969[a]

Type of stationary engine	Supercharged	Fuel	Estimated total hp, millions	Reference	Oxides of nitrogen emissions, lb NO_x/lb fuel	Oxides of nitrogen emissions, lb $NO_x/10^6$ Btu
Reciprocating engine						
Diesel, precomb. chamber[b]	Yes	Oil	0.7		(0.02)	(0.9)
Diesel, precomb. chamber	No	Oil	0.1	4	0.007-0.010	0.38-0.55
Diesel, direct injection	Yes	Oil	14	5	0.07	3.8
Diesel, direct injection	No	Oil	2	4,5,6,7	0.021-0.047	1.2-2.6
Gas engine, spark ignited	Yes	Gas	45		(0.16)	(8.0)
Gas engine, spark ignited	No	Gas	8	8	0.084	4.0
Gas turbine						
Turbojet	--	Oil	5	9	0.008-0.01	0.11-0.32
Turbojet	--	Gas	46		(0.004)[b]	(0.2)[b]

[a] Estimated figures in parentheses are based on assumption that supercharging doubles NO_x emissions.

[b] Estimates are based on assumption that gas will emit the same amount of NO_x as turbo fuel. This may be open to question, and probably penalize the turbojet engine. If the turbine engine responded to gas fuel in the same way as the diesel engine, NO_x emissions would be of the order of 0.04 lb/million Btu, a very low air pollutant emission level.

Table 5-4. SUMMARY OF SOURCE SAMPLING TESTS FOR TWO DUAL-FUEL (GAS AND DIESEL) ENGINES

Fuel	Engine 1		Engine 2	
	Diesel No. 2	Natural gas	Diesel No. 2	Natural gas
Airflow, lb/hr	39,291	31,767	21,639	19,813
Air/fuel ratio	35.6	31.5	33.0	34.6
Exhaust flow, scfm[a]	8,890	7,350	4,910	4,540
NO_x, lb/lb fuel	0.074	0.075	0.066	0.038
NO_x, lb/10^6 Btu	4.04	3.50	3.61	1.77
NO_x, ppm	1,375	1,544	1,251	746
Percent rated load	77		80	
Brake horsepower	3,185		1,850	
Brake mean effective pressure, psi	105		160	
Engine speed, rpm	360		514	

[a] 29.92 in. Hg, 60°F.

emissions from stationary engines may be possible. Applicability to both reciprocating piston engines and turbine engines is discussed.

5.2.1.2.1 Combustion Chamber Design–The beneficial effect of the precombustion chamber (Table 5-5) suggests that combustion chamber design and modification may have a significant effect on NO_x emissions. The precombustion chamber provides a type of two-stage combustion, the first stage under extremely rich fuel conditions and the second stage, very lean. It can be applied readily to oil-fired piston engines. It does not seem to be as easily adapted to the gas-fired type. Initial cost of the engine may be increased slightly, and there may be an adverse effect on thermal efficiency if the engine is operated under conditions differing from optimum design. Examples of precombustion chamber engine designs are the Caterpillar, the M.W.M. (Motoren-Werke Mannheim), the Mercedes-Benz OM-621, and the larger Daimler-Benz diesels.

Other combustion chamber modifications that may influence NO_x emissions and require further investigation include the use of turbulence chambers, as used in engines manufactured by International Harvester, Waukesha, John Deere, and Deutz, and "energy cells," as used in Minneapolis-Moline engines. Energy cells provide controlled combustion to prevent high peak pressures and rough operation.

5.2.1.2.2 Fuel Type–There are some indications that by increasing fuel API gravity (i.e., decreasing specific gravity) a decrease in NO_x emissions occurs in a diesel engine, as shown in Table 5-5. NO_x production decreases about 25 percent when the gravity of the fuel is increased from 30.9 to 42.8° API. This trend is also supported by the low emissions obtained with natural gas. There are, of course, accompanying changes in boiling range, viscosity, and cetane number; the latter effect is probably significant also. It is not clear which is the controlling variable, although the mid-boiling point, or viscosity, gives the most consistent trend. Thus it appears that it may be possible to modify NO_x emissions by tailoring fuel properties. It will be appreciated, however, that the use of special fuels will add to fuel costs because of problems associated with availability, refining, and marketing.

5.2.1.2.3 Exhaust Recycle–This method has been shown to be an effective means of controlling NO_x emissions in gasoline engines, furnaces, etc.[12] It may also reduce NO_x from diesel engines if the fresh air-to-fuel ratio is held constant, but testing will be required to confirm this. It will probably mean a decrease in the maximum power capability of the

Table 5–5. EFFECT OF FUEL TYPE ON EMISSIONS OF NO_x FROM STATIONARY DIESEL ENGINE[a]

Fuel characteristics						NO_x emissions,		
° API	FIA Anal., Percent Aromatics	Est. net heat. value Btu/lb	Boiling Point °F 50% dist.	Boiling Point °F Final Final	Viscosity S.U.S. @ 100° F	lb NO_x/lb fuel	lb $NO_x/10^6$ Btu	Reference
42.8	12	18,570	428	514	33.0	0.023	1.24	4
32.7	28	18,300	400	609	34.3	0.023	1.26	4
32.4	--	18,290	519	561	36.1	0.03	1.64	4
30.9	26	18,220	538	656	38.0	0.03	1.65	4
Methane	0	21,500	259	---	---	0.0056[b]	0.26[b]	8

[a] Precombustion chamber, turbo-charged, rated speed, about 25 to 1 air fuel ratio.

[b] Actual data doubled to correct for turbo-charging; data at full throttle, 72% Max. IMEP and 72% stoichiometric fuel, i.e., A/F = 24.

engine and will involve a modest increase in cost since additional piping and a control mechanism will be needed.

5.2.1.2.4 Optimum Air/Fuel Ratio–The maximum power setting of most stationary diesel engines is limited by smoking at about a 20-to-1 air/fuel ratio.

It is possible, therefore, to vary the air/fuel ratio only by reducing the amount of fuel injected, which results in a proportional increase in the air/fuel ratio and a corresponding decrease in power. The indications are that as fuel rate is reduced, NO_x emissions in pounds per hour are a linear function of power.[14] This means that the rate of NO_x formation per pound of fuel (or million Btu) is constant over the range in which specific fuel consumption is constant and no benefit results from the overalll leaner or higher air/fuel operation.

Gas engines, on the other hand, are usually set at an air/fuel ratio giving maximum economy of operation; about 2.5 percent excess oxygen equivalent to about 19-to-1 air/fuel ratio. As shown in Table 5-6, this is very close to the conditions at which maximum NO_x production is obtained. Table 5-6 also indicates that NO_x production can be reduced by changing to either richer or leaner operation. Using richer mixtures creates the risk of increasing the emissions of unburned hydrocarbons and CO. This hazard can be avoided by using higher air/fuel ratios. For example, with methane it is possible to operate with only 70 percent of the stoichiometric amount

Table 5–6. EFFECT OF AIR/FUEL RATIO[a] ON NO_x PRODUCTION IN SPARK-IGNITED STATIONARY GAS ENGINES[13]

Stoichiometric fuel, %	Mixture, lb air/lb fuel	Power, % max. IMEP	NO_x production lb NO_x/lb fuel	NO_x production lb $NO_x/10^6$ Btu
100	17.1	88.9	0.038	1.8
95	18	---	0.065	3.0
92	18.6	---	0.095	4.4
87	19.7	80	0.069	3.2
84	20.4	78	0.055	2.6
70	24.4	71	0.028	1.3
65	26.3	misfire	---	

[a] Full throttle; maximum power spark, 1,000 rpm; compression ratio, 8/1; fuel, methane.

of fuel without misfiring the engine. At this point, NO_X emissions are reduced to about 30 percent of their maximum value. The penalty for this type of operation is a loss of power (e.g., 30 percent at 70 percent stoichiometric fuel) equivalent to a 30% increase in the initial cost of an engine.

The reason that adjustment of air/fuel ratio controls NO_X emissions in gas engines and not in injected diesels is because the gas engine operates with a premixed, homogeneous air/fuel mixture. Thus, flame temperatures are reduced at high air-to-fuel ratios. This is not the case with the heterogeneous air-fuel mixture present in a diesel engine in which liquid fuel is sprayed into the air in the combustion chamber and combustion takes place in fuel-rich places.

5.2.1.2.5 Modification of Fuel Injection Timing–It is possible to vary the pressure and temperature conditions in a fuel-injection diesel engine by changing the timing of the fuel injection, by changing the point in the cycle at which fuel injection is started and/or the rate of fuel addition. Two-stage fuel injection is also a possibility. The effect of these variables on NO_X production as well as power output and/or thermal efficiency requires clarification.

5.2.1.2.6 Variable Compression Ratio–Variable compression ratio-compression ignition engines have been developed for the military.[11] The compression ratio is changed by hydraulically raising or lowering the height of the piston. The pistons are undoubtedly more expensive than the conventional type and may require somewhat more maintenance. Such a system tends to maintain a preset peak combustion pressure in the combustion chamber. Presumably this would avoid the excessively severe cycles which occur frequently[15] in the conventional diesel engine and cause a disproportionate part of the NO_X emissions. The NO_X emission characteristics of the variable- compression engine are thus of considerable interest.

5.2.1.2.7 Treating Exhaust–NO_X can, of course, be controlled by removal from the exhaust gases. The various possibilities would be analogous to the methods developed for stack gas treatment previously described.[12] Complicating factors peculiar to the diesel engine may be the larger amounts of air used in the diesel cycle (30 percent or more above stoichiometric requirements) and a relatively low exhaust temperature. Adding control equipment to an engine for exhaust treatment will obviously increase both initial costs and operating costs.

5.2.2 Turbine Engines

Gas turbine engines in stationary applications in the U.S. are estimated to have a total current capacity of 51 million horsepower (based on Reference 12 assuming 60 percent of the worldwide stationary turbine population is in the U.S.). Approximately 90 percent of these engines are fueled with natural gas.

5.2.2.1 Emissions

Emissions of NO_X from a turbojet engine are already quite low, about one-tenth those of a diesel engine. Even correcting for a difference in thermal efficiency (20 versus 30 percent), a gas turbine would presumably emit only about one-sixth of the NO_X emitted by a diesel. Further improvements can be made, however, and may be worthy of consideration if costs, in terms of not only money but economy, performance, and the like, are not too high.

5.2.2.2 Control Techniques

5.2.2.2.1 Combustion Chamber Design–Exhaust recirculation has been previously reported[12] as capable of making marked reductions in NO_X emissions in an oil-fired domestic heater. It would seem possible that an analogous type of recirculation could be developed within the combustor of a gas turbine engine, with similar benficial effects on NO_X emissions.

Two or more stage combustion is also an effective general method for holding down NO_X formation. In this type of operation, partial combustion is carried out initially in a fuel-rich primary zone; combustion is then completed by the addition of more air. The beneficial effect is probably due to keeping combustion temperatures down and restricting the availability of oxygen during the critical combustion phases.

It appears, therefore, that studies of combustor design directed toward encouraging internal exhaust recirculation and controlling oxygen availability would be fruitful approaches to reducing NO_x formation in turbine engines. While such studies have not yet been reported, it is believed that improved combustors could be developed without any major increase in cost. The effect of design changes on turbine performance criteria needs to be studied to determine what penalties would be involved by this approach.

5.2.2.2.2 Effect of Fuel Composition–It is well known that the radiation characteristics of a flame in a gas turbine engine increase as the hydrogen content of the fuel is decreased. This suggests that the temperature of the flame from a fuel with low hydrogen content may be lower, because of increased radiation to the combustor walls, than that from a fuel containing more hydrogen. NO_x emissions in turbine engines may thus vary with fuel characteristics. Data are required. It is understood, of course, that the use of special fuels usually results in an increase in fuel cost.

5.2.2.2.3 Treatment of Exhaust–The considerations in treating exhaust gases from a turbine engine are essentially the same as the diesel engine, with the added complication that the turbine utilizes about twice as much air.

5.2.2.2.4 Reduction of Turbine Inlet Temperature–Gas turbine efficiency depends directly on the differences in temperature between the inlet and outlet gas; any change that lowers the inlet temperature requires a larger turbine for a given power output.

It is possible that NO_x emissions can be lowered by reducing turbine inlet temperatures. For example, observations demonstrate that the NO_x level is determined by the degree of progress of the formation reaction at the time of thermal quenching.[16] It appears that at low turbine inlet temperatures this quenching occurs earlier in the formation reaction than at higher turbine inlet temperatures (Table 5-7). The drop in NO_x formation at the higher air/fuel ratios (i.e., lower turbine inlet temperature) is probably because of the larger quench air ratio (higher excess air/fuel ratio).

This effect requires clarification. The penalties for such a step, however, are reflected in installation and operating costs. It is estimated that a 100° F decrease in turbine inlet temperature will decrease power by 10 percent and will increase fuel consumption by about 5 percent.

5.2.3 Costs

Little information is available on the costs of reducing NO_x emissions from stationary engines.

5.2.3.1 Diesel Engines

Currently, the only effective way to reduce NO_x is to use engines with design features that tend to minimize NO_x production.

Table 5–7. EFFECT OF AIR/FUEL RATIO[a] ON NO_x FORMATION IN EXPERIMENTAL COMBUSTOR RIG[16]

Air/fuel ratio, lb air/lb fuel	Relative temperature at exit of combustor, °F	NO concentration, ppm		Calculated NO_x, lb/lb fuel
		As measured	Corrected to 15/1 air/fuel	
53	T	34	120	0.0017
73	T minus 370	10	50	0.0007

[a] Directly related to temperature of gases at combustor exit.

Engines employing precombustion chambers, which minimize NO_X, may have slightly higher initial costs and fuel consumption than engines without precombustion chambers. The magnitude of the cost differential would have to be established by obtaining price quotations for specific applications.

5.2.3.2 Gas Engines

Reduction in NO_X by increasing air/fuel ratio from the optimum power setting decreases power output by as much as 30 percent. This would, in turn, increase original engine costs by as much as 30 percent.

Water injection into the intake manifold of gas engines has promising potential for NO_X removal. The initial cost of a system for water injection was roughly estimated at $2,000 per engine. With water costs of 20¢ per thousand gallons, the costs of reducing NO_X emissions would be as given in Table 5-8.

Table 5-8 shows very high costs per unit of NO_X removed for small engines, and low costs for large engines. The costs are based on 20 percent capital charges, an injection rate of 1.25 pounds of water per pound of fuel, and 75 percent reduction in NO_X.

Table 5–8. NITROGEN OXIDE CONTROL COSTS FOR STATIONARY GAS ENGINES

Engine, hp	Cost, $/yr	Cost, $/ton NO_X eliminated
80	60.00	420.00
800	800.00	9.30
4,200	930.00	1.20

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6. OTHER COMBUSTION PROCESSES

Major amounts of the total fuels burned and NO_x emissions released in the United States are associated with small-scale combustion processes. These include important nonindustrial uses in domestic and commercial heating, hot water supply, a wide variety of incinerators, and burning of solid wastes. This is a much larger stationary use of fuels than the electric utilities, but it is a less intense type of combustion. Its contribution to NO_x is significant, particularly in residential areas.

"Commercial" in this discussion denotes multiple-unit heating and small appliances used in business, which are similar to household equipment and appliances such as space and water heaters, ranges, and clothes dryers.

6.1 DOMESTIC AND COMMERCIAL HEATING

Some 30 percent of the total fossil fuels used in the United States for energy production (transportation excluded) is consumed in domestic and commercial heating. This represents $12{,}432 \times 10^{12}$ Btu annual consumption, and it substantially exceeds the $9{,}994 \times 10^{12}$ Btu required for power generation by the electric utilities.[1]

Limited statistics[2] for the breakdown into fuel types within this sector show the following division for the approximately 29 million domestic, automatic central-heating units in use in 1967: gas burners, 18,184,321; oil burners, 10,692,825; and coal stokers, 263,964.

The amount of fuel consumed[3] in 1966 for space heating and cooking only is shown in Table 6-1 by fuel type and equivalent Btu content.

The use of gas in the United States for domestic purposes only was estimated,[5] as of January 1968, as shown in Table 6-2.

Table 6-2 statistics show the extremly large

Table 6–1. FUEL CONSUMPTION FOR SPACE HEATING AND COOKING, 1966

Fuel type	Quantity	Equivalent heating value,[4] 10^{12} Btu
Natural gas, 10^9 ft^3	5,761	5,945
Distillate fuel oil, 42-gal bbl	472,778,000	2,832
Residual fuel oil, 42-gal bbl	167,471,000	1,052

Table 6–2. GAS CONSUMPTION FOR DOMESTIC HEATING IN UNITED STATES

Number of customers	Type of use	Avg heat use, 10^5 Btu/unit-yr	Total heat use/yr, 10^{12} Btu
28,800,000	Heating units (1 and 2 family)	1,020	2,938
33,000,000	Hot water	300	990
38,200,000	Ranges	100	420
Total			4,348

number of NO_X emitters involved in the domestic and commercial heating categories, and the substantial quantities of fuel used.

6.1.1 Emissions

The rate at which fuel is used for domestic appliances, such as water heaters, ranges, gas refrigerators, and clothes driers, remains reasonably constant throughout the year, but a much larger amount is required for space heating during the 6-month winter period. Thus, the rate of domestic fuel consumption increases during the winter over the average percentage consumed annually; in mid-winter months, in many areas, it can be well over 50 percent of all fossil fuels consumed.

The contribution of residential space heating to NO_X is suggested by data on seasonal and diurnal effects on fuel usage for space heating from the Continuous Air Monitoring Projects (CAMP) and other sources, which indicate that the variations in SO_2 emissions in urban areas may be correlated with changes in residential heating throughout the day and throughout the year.[6,7,8]

Significantly, the products of domestic combustion are vented close to ground level. Under adverse conditions such as stagnation or aerodynamic downwash, these gases become an immediate part of the ambient atmosphere. The extent of this pollution is not as visible with clean burning gas and oil fuels as chimney soot was in the past, when coal was the main fuel, but the NO_X and other less visible combustion products formed are still present. Data from CAMP and other studies pointed out that chimney gases are poorly dispersed; this means that a given amount of NO_X at ground level will have a greatly aggravated effect on ambient air compared to the same amount emitted from a tall utility stack. The air layer into which the combustion gases are distributed is thinner at ground level, and under adverse conditions this may be significant. Commercial buildings and apartments will presumably show an intermediate effect.[8]

The effect of unit size and severity of operation report by Mills[9] et al. from Los Angeles data has a direct bearing on NO_X emissions from domestic heating units (see Section 3). According to their correlation (Figure 3-1), a typical gas-fired domestic furnace of 150,000 Btu capacity produces NO_X at about 12 percent of that produced in a large utility boiler of 10^{10} Btu, for a given amount of fuel. A similar ratio exists for oil-fired equipment. Although domestic and commercial heating units consume some 125 percent of the fuel used in utility boilers, their total contribution to NO_X in the United States will be only 12 percent of this ratio, or about 7 percent of all NO_X in the United States, compared to 44 percent for the utilities.

6.1.2 Control Techniques

The combustion modifications discussed above (see Sections 4.1 and 5.1) as promising control techniques are theoretically applicable to small domestic heating units, but there are serious obstacles to their practical use. The trend, in fact, is in the other direction, since high efficiency and compact size in the design of modern domestic units lead toward more intense, concentrated, and high-turbulence flames. The result is a higher flame temperature, and inherently more NO_X per unit of heat released.[10] Many domestic installations are improperly installed, out of adjustment, or poorly maintained, particularly in regard to the cleaning of flues and chimneys. The problem has been serious in European cities, as well as in the United States.[11] Concerted action by the public is required if the problem of faulty and poorly maintained installations is to be solved.

The specific modifications considered most promising (low excess air, flue gas recirculation, two-stage combustion, and water injection), all require additional equipment and operating controls. Modifications for each unit are expensive; the smaller the unit, the more expensive these controls will be compared to total unit cost. Modifications other than proper adjustment are less expensive and are easier to apply in new installations; design and engineering research is required to develop such new equipment.

The trend in small boiler operation is toward automatic controls. Although certain of the above modifications for NO_X control, such as burner design and placement, can be built into automatic boilers, other features will increase the complexity of operation. Such problems could make safety the determinant factor.

Multiple-unit structures, such as apartment buildings, schools, and commercial houses, in the larger northern cities require heating plants of up to 500 horsepower rating. Combustion modifications are more practical in this size range for NO_X reduction. Such control means are discussed in full in Section 5.2 above.

A partial reduction in NO_X can be realized by converting from coal to other fuels. This conversion is substantially complete in most areas, so that there is little room for further improvement in this direction. The NO_X emissions factors for oil and natural gas in household-size units are not sufficiently different to justify any preference for either fuel on this basis (see Sections 3.1 and 5.2.1).

Domestic NO_X emissions may also be controlled by conversion to electrical heat, which transfers the problem to the big utility plant, where controls can be more effective. In 1967, there were approximately 2,486,000 automatic, domestic, electric heating installations versus 29 million gas- and coal-fired installations.[2] Electricity can be used for all space heating, cooking, hot water heating, clothes drying, etc., and it has advantages in overall safety and convenience. On the other hand, it is sometimes the most expensive source of heat energy. Low-pressure waste steam from large utility plants is also being used for heating and refrigeration in various urban areas in place of fossil fuels.

In general, in the domestic and commercial sectors, the smaller the heat output, the more numerous are the sources and the more difficult is the control of NO_X emissions. Electric heating has the virture of not contributing to emissions from individual sources; and its use is expected to increase, particularly in densely populated areas.

6.2 INCINERATION AND OTHER BURNING

Preliminary results of a survey conducted by the Public Health Service indicate tnat household, commercial, and industrial solid waste production in the United States is about 10 pounds per capita per day, or 360 million tons per year. About 190 million tons per year (or 5.3 pounds per day per capita) is collected for disposal, and the remainder is either disposed of on site or handled by the household or establishment itself.[12] An estimated 177 million tons of this material is burned in the open or in incinerators.[13] An additional 550 million tons of agricultural waste, 1.1 billion tons of animal wastes, and 1.5 billion tons of mineral wastes are generated each year.[12] It is estimated that half of the agricultural wastes are burned in the open and that, except for 48 million tons of coal refuse consumed by fire each year, no animal or mineral wastes are burned.[13] The quantities of material consumed by forest burning and structural fires are estimated to total about 200 million and 8 million tons a year, respectively.[13]

Incineration and open burning are used to reduce the weight and volume of solid waste. High-temperature incineration with excess air reduces emissions of particulate matter, carbon monoxide, and smog-forming compounds such as aldehydes, hydrocarbons, and organic acids, which typify open burning, but it tends to increase nitrogen oxide emissions.

6.2.1 Emissions

Estimated NO_X emissions from incineration and other burning are shown in Table 6-3.

NO_X levels in incinerator flue gases are in the range of 50 to 80 ppm,[14] and 8 to 130 ppm in gas from open burning, where the NO_X level varies with cycle time.[15] Emission factors and the volumes of various solid wastes consumed in each disposition are difficult to measure, particularly for open burning. The factor for open burning appears high relative to factors for incineration, since it does not seem reasonable that open burning, in which radiation to the sky cools the flame,

Table 6–3. ESTIMATED NATIONAL EMISSIONS FROM INCINERATION AND OTHER BURNING, 1968[13]

	Quantity, 10^6 tons/yr	NO_x emission, 10^3 tons/yr
On-site incineration	57	69
Municipal incineration	16	19
Conical burner incineration	27	18
Open burning	77	450
Agricultural burning	275	280
Controlled forest burning	76	400
Forest wildfires	146	800
Structural wildfires	8	23
Coal refuse fires	48	190
Total	730	2,249

would produce more NO_x than combustion in a closed system (see Section 8).

6.2.2 Control Techniques

The use of waste dispositions other than combustion may be the most likely means for reducing NO_x emissions. since the methods normally used for control of other emissions from incineration, such as particulate matter, organics, and carbon monoxide, tend to increase emissions of NO_x. The reduction of NO_x emissions by some of these methods and by changing combustion conditions in incinerators is discussed below.

6.2.2.1 Waste Disposal

From the standpoint of air pollution, the least satisfactory method of waste disposal is burning. Sanitary land fills are good alternatives, to the extent that land usable for this purpose is available. Approximately 1 acre-foot of land is required per 1,000 persons per year of operation when waste production is 4.5 pounds per day per capita.[16] In addition, cover material approximating 20 percent by volume of the compacted waste is required; the availability of cover material may limit the use of sanitary land fill.

Unusual local factors may lead to a solution of the land fill site problem. One reference[17] indicates that in a pilot project under way the refuse is shredded and baled for loading on rail cars for shipment to abandoned strip-mine land-fill sites.

Other noncombustion alternatives may have application in some localities. Composting is now being tested on a practical scale,[18] and hog feeding has been used for disposal of garbage. Dumping at sea has been practiced by some seacoast cities, but some of the garbage floats and returns to shore unless dumped at appreciable distances. Such practices are now forbidden by the Federal Government. Elsewhere, refuse has been ground and compressed into bales, which are then wrapped in chicken wire and coated with asphalt.[19] The high-density bales sink to the bottom in the deeper ocean areas and remain intact. The practice of grinding garbage in kitchen units and flushing it down the sewer has been increasing. This in turn increases the load of sewage disposal plants and the amount of sewage sludge.

Incinerators that reduce NO_x by changing combustion conditions are not available except on a developmental basis. Most incinerators are not provided with means to remove the heat of combustion. Accordingly, the burning rates must often be curtailed and overfire air provided in order to protect the incinerator from heat damage. Gas temperature must exceed 1,400° F if carbon particles, organics, carbon monoxide, and odorous compounds are to be consumed. Temperatures in excess of 1,800° F cause sintering of ash particles, which can cause undesirable accumulations.[20]

Data are rather firm in showing that excess air increases NO_x emission regardless of the cooling effect it has on the gas temperature. An increase from 50 to 300 percent of excess air caused a 32 percent increase in NO_x per pound of waste burned.[21] Rose and coworkers[5] showed that an average value of 1.96 pounds of NO_x emitted per ton of waste of 50 percent excess air, and 2.19 at 150 percent of excess air, an increase of 12 percent. Also, an increase in gas temperature from roughly 1,500° to 2,300° F caused the NO_x concentration to increase from 50 to 100 ppm. As expected, feed rate also increased the emission of NO_x per unit weight of waste.

Auxiliary fuel may be used in certain incinerators for such purposes as waste drying, startup, supplemental heat, and afterburning. Either oil or gas is used, and the NO_x emitted is, in part, from the auxiliary fuel. For example, in one domestic garbage incinerator[22] designed for low particulate and organic emissions, natural gas was burned to increase heat input to 15,000 Btu per pound of waste as compared with a heating value for garbage on the order of 2,500 Btu per pound. The NO_x emissions from burning 12.5 cubic feet of gas per pound of garbage are estimated at 2.9 pounds per ton of garbage, which is a very substantial increase as compared with estimates of emissions without gas burning on the order of 1 pound per ton.[23] Figures for a flue-fed incinerator[23] are 10 pounds of NO_x emitted per ton with an afterburner and 0.3 without. These data suggest that the NO_x emission from the incineration of refuse is substantially increased by the auxiliary firing of oil and gas fuels.

Heat may be recovered from incinerators by steam boilers, thus furnishing energy that would otherwise have to be generated by burning fossil fuels. Total NO_x emissions are thus reduced according to the amounts of fossil fuel not burned. This means of refuse disposal has already received considerable attention in Europe,[24-28] and some attention in the United States.

6.2.2.2 Forest Wildfires

An estimated 800,000 tons of nitrogen oxide is emitted annually from forest wildfires.[13] These fires are caused by natural elements such as lightning or by carelessness. Considerable activity has been and is being directed toward reducing the frequency of occurrence and the severity of these fires. These activities include publishing and advertising information on fire prevention and control, surveillance of forest areas where fires are likely to occur, and various fire-fighting and control activities. Information on forest fire prevention and control is available from the U.S. Department of Interior and from state and local agencies.

6.2.2.3 Controlled Vegetation Burning

Forest debris, crop residues, scrub, brush, weeds, grass, and other vegetation are burned for one or more of the following purposes:

1. To control vegetation, insects, or organisms harmful to plant life.
2. To reduce the volume of waste.
3. To minimize fire hazards.
4. To improve land.

NO_x emissions from this burning are estimated to be slightly less than 700,000 tons per year.[13]

Because collection and incineration of these materials would tend to increase NO_x emissions, the only current way to control emissions is to avoid combustion. In the future it may be possible to develop incineration processes that can control NO_x and other emissions, as well as particulate matter, organics, odorous compounds, and carbon monoxide; or it may be possible to develop equipment that can burn these materials as substitutes for fossil fuels.

Other alternatives to incineration are abandonment or burying at the site, transport to and disposal in remote areas, and utilization. Abandonment or burning at the site is practical in cases where no other harmful effects will ensue. Abandoned or buried vegetation can have harmful effects upon plant life by hosting harmful insects or organisms, for example. Agricultural agencies such as the

U.S. Department of Agriculture, or state and local agencies should be consulted before these techniques are employed. Other harmful aspects such as odor or water pollution potential, or fire hazards, must also be considered. Disposal of waste materials in areas where harmful effects are avoided is possible, but is not commonly practiced. Some of these waste materials can be used. Larger forest scraps are processed by chipping or crushing and are used as raw materials for kraft pulp mills or for processes producing fiberboard, charcoal briquettes, or synthetic firewood.[19] Composting or animal feeding are other possible alternatives to burning.[18]

6.2.2.4 Coal Refuse Fires

An estimated 190,000 tons of NO_x is emitted each year from 19 billion cubic feet of burning coal refuse.[13] Extinguishing and preventing these fires are the techniques used for eliminating these emissions. These techniques involve cooling and repiling the refuse; sealing refuse with impervious material; injecting slurries of noncombustibles into the refuse; minimizing the quantity of combustibles in refuse; and preventing ignition of refuse. These techniques and the status of future plans and research are described and discussed in the document, *Control Techniques for Sulfur Oxide Air Pollutants.*[30]

6.2.2.5 Structural Fires

Structural fires emit an estimated 23,000 tons of NO_x annually.[13] Prevention and control techniques are used to reduce these emissions. Use of fireproof construction, proper handling, storage, and packaging of flammable materials; and publishing and advertising information on fire prevention are some of the techniques used to prevent fires. Fire control techniques include the various methods for promptly extinguishing fires: use of sprinkler, foam, and inert gas systems; provision of adequate fire-fighting facilities and personnel; and provision of adequate alarm systems. Information on these and other techniques for fire prevention and control are available from agencies such as local fire departments, National Fire Protection Association, National Safety Council, and insurance companies.

6.2.3 Costs of Control

Where substitution of noncombustion alternatives for incineration is the most practical means of controlling NO_x emissions, costs of controls are a function of the relative costs of noncombustion disposition and incineration. The costs reported vary widely with locality.

Sanitary landfill costs, including amortiza tion, have been reported as $1.05 per ton for 27,000 tons per year of refuse and $1.27 per ton for 11,000 tons per year.[12] The costs do not include costs of collection and transportation to the site. Operating costs for incineratons are $4 to $8 per ton of refuse;[31] estimated capital costs are $6,000 to $13,000 per ton per day.[32] Sanitary landfill is less costly than incineration. A report from Philadelphia has estimated that the disposal of refuse by railroad shipment to available abandoned coal mines would cost $2.00 per ton less than incineration.[17]

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7. INDUSTRIAL AND CHEMICAL PROCESSES

Nitrogen oxides are a minor source of air pollution, incidental to combustion heat, for a number of industrial processes having more serious problems due to emissions of smoke, particulates, SO_2, or organic chemical wastes. For example, several large industries such as nonferrous mineral producers or pulp and paper mills have problems with SO_2, but no particular concern with NO_x. Some industrial processes that emit only a small percentage of total national emissions could cause dangerous local concentrations, if uncontrolled.

The problem of NO_x emissions has been researched in the chemical industry more intensively than anywhere else because it may represent the loss of a valuable raw material. The following sections of this report discuss commercial processes developed for NO_x control in the manufacture and uses of nitric acid.

The NO_x released in vent gases from the manufacture and industrial uses of nitric acid differs markedly from that emitted from a combustion flue gas in concentration, total amount, and the ratio of NO_2 to NO present. The NO_x-containing chemical gas is commonly a process stream which must be recycled with maximum NO_x recovery in order to have an economical process. Vent gas is released only because it is too impure to recycle or too low in concentration for economic recovery. The economic limit with a pure gas, as in nitric acid manufacture, is about 0.1 to 0.3 percent NO_x, or 1,000 to 3,000 ppm. The limit is higher in organic nitrations, such as the manufacture of nitroglycerine, where NO_x content of the vent gas may approach 1 percent NO_x, or 10,000 ppm.

The total amount of NO_x emitted from all chemical manufacturing is about 1 percent of all NO_x from man-made sources in the United States. These processes represent a local nuisance problem only in special local areas. The problem has been most serious in military ordnance works, which manufacture large volumes of nitric acid and use it in organic nitrations. A single plant like the Volunteer Ordnance Works has produced, for example, emissions of NO_x equal to all nonmilitary uses of nitric acid in the United States.

A high ratio of NO_2/NO at high concentration causes the gases to be visible as a brownish plume. The visibility limit depends on the total amount of NO_2 present in the gas volume or layer observed. A convenient rule of thumb is that a stack plume or air layer will have a visible brown color when the NO_2 concentration exceeds 2,400 ppm divided by the stack diameter in inches.[1] This means that the threshold of visibility for a 2-inch-diameter stack is about 1,200 ppm of NO_2 and for a 1-foot-diameter stack, 200 ppm of NO_2 (or 2,000 ppm of NO_x at a 1:10 ratio of NO_2:NO).

The distinction between NO_2 concentrations and total amount can be quite important in chemical vent gases, since a short burst of NO_2 at 10,000 ppm may be visible but less hazardous than many times as much NO_x emitted from a large stack at a lower concentration. The total amount in a short, concentrated emission may be too small to have a detectable effect on NO_x levels in ambient air.

A large amount of research with varying degrees of success has been carried out on the development of processes for the removal of NO_x from the off-gas resulting from the manufacture and uses of nitric acid. The following processes are discussed in detail in Sections 7.1 and 7.2 below, and summarized briefly here to show their general relationship.

Catalytic reduction reduces NO_2 to NO and in some cases NO to N_2, using a reducing gas such as methane, hydrogen, or carbon monoxide. The best catalysts to date are noble metals, which are so sulfur-sensitive that this process cannot be used with many impure industrial gases.

Catalytic decolorization and power recovery is a form of catalytic reduction in which the fuel oxidized reduces the NO_2 present to colorless and nonirritant NO. This is a highly exothermic process, requiring careful temperature controls, in which the heat released provides power. Recovery of the heat energy in a turboexpander enables the manufacturer to break even on costs.

Nonselective catalytic abatement requires enough added reducing fuel to burn out the oxygen in the tail gas and then to reduce both the NO_2 and NO present to N_2. This is much more difficult technically than decolorization, and commercial results have been less satisfactory than decolorization. It requires equipment and provisions for interstage or product heat removal.

Selective catalytic abatement involves the direct reduction, within a narrow temperature range, of NO_x to molecular nitrogen by ammonia. This reduction is specific for NO_x and occurs without the simultaneous reaction with the oxygen in the flue gas. The process has been only partly successful to date and requires further development.

Caustic scrubbing, lime-water, or a limestone slurry can remove NO_2 or a 1:1 mol ratio of NO_2/NO (equivalent to N_2O_3), but this can create a serious problem of waste water disposal and this method is in only limited use.

Adsorbents or absorbents have a limited capacity. Molecular sieve adsorbents are offered commercially for the removal of NO_x from a moisture-free gas. Available information indicates that the development of a process of this type applicable to combustion flue gases is unlikely.

NO_x incineration is a noncatalytic reduction process in which a fuel is added in at least 10 percent excess over the amount corresponding to the NO_x and oxygen present, and the NO_x is reduced to N_2.

Details of these control methods are discussed in Sections 7.1.2, 7.2.2.2, and 7.2.3.2 in connection with specific processes to which they may be applied.

Dilution of NO_x tail gases in the stack with large volumes of air makes the effluent less visible; but, because dilution has no effect on source strength, it has little or no effect on ground-level concentration. Addition of diluent air, however, increases stack velocity, which increases effective stack height and, to this extent, contributes to decreased ground-level NO_x concentrations.

7.1 NITRIC ACID MANUFACTURE

All nitric acid manufactured in the United States is made by the catalytic oxidation of ammonia. Air and ammonia are preheated, mixed, and passed over a catalyst, usually platinum-rhodium. The following reaction occurs:

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \quad (1)$$

The steam is cooled to 100°F or less, and the NO then reacts with more oxygen to form nitrogen dioxide and its liquid dimer, nitrogen tetroxide.

$$2NO + O_2 \rightarrow 2NO_2 \rightleftharpoons N_2O_4 \quad (2)$$

NO_2 is a reddish-brown gas with a sharp odor.

The liquid and gas then enter an absorber tower. Added air is directed to the bottom of the tower and water to the top. The NO_2 (or N_2O_4) reacts with water to form nitric acid and NO, as follows:

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO \quad (3)$$

The formation of 1 mole of NO for each 2 moles of HNO_3 makes it necessary to reoxidize NO after each absorption stage since the gas rises up the absorber and limits the level of recovery that can be economically achieved.

Acid product is withdrawn from the bottom of the tower in concentrations of 55 to 65 percent. The air entering the bottom of the tower serves to strip NO_2 from the product and to supply oxygen for reoxidizing the NO formed in making nitric acid (equation 3).

Normally, pressures of 80 to 120 pounds per square inch (psi) are employed in the oxidation and absorption operations. Tail gas from the absorber passes through an entrainment eliminator for removal of nitric acid mist. Tail gas is then reheated by exchange with the gases from ammonia oxidation and is directed to a turboexpander for energy recovery.

Before corrosion-resistant materials were developed, the ammonia oxidation and absorber operations were carried out at essentially atmospheric pressure. Because of the low absorption and NO oxidation rates, much more absorption volume was required, and several large towers were placed in series. Some of these low-pressure units are still in operation, but they represent less than 5 percent of the current United States nitric acid capacity.[2] Improved technology has made the "pressure process" more economical, and it is the preferred process in the United States, so that over 90 percent of our nitric acid plant capacity is believed to be of the pressure type.[2] A typical flow plan is shown in Figure 7-1. Except for leaks, the only source of NO_x emissions is the tail gas from the unit.

Combination pressure plants carry out the ammonia oxidation step at low pressure and absorption at high pressure. Intermediate-pressure plants carry out both operations at intermediate pressures.

For most uses, the 55 to 65 percent nitric acid made by ammonia oxidation is satisfactory. For some uses, however, high-strength acid is required. These requirements are met by concentrating the lower strength acids.

Figure 7-2 illustrates a nitric acid concentration unit using extractive distillation with sulfuric acid. A mixture of strong sulfuric acid and 55 to 65 percent nitric acid is introduced at the top of a packed column, and flows down the column countercurrent to the ascending vapors. Nitric acid leaves the

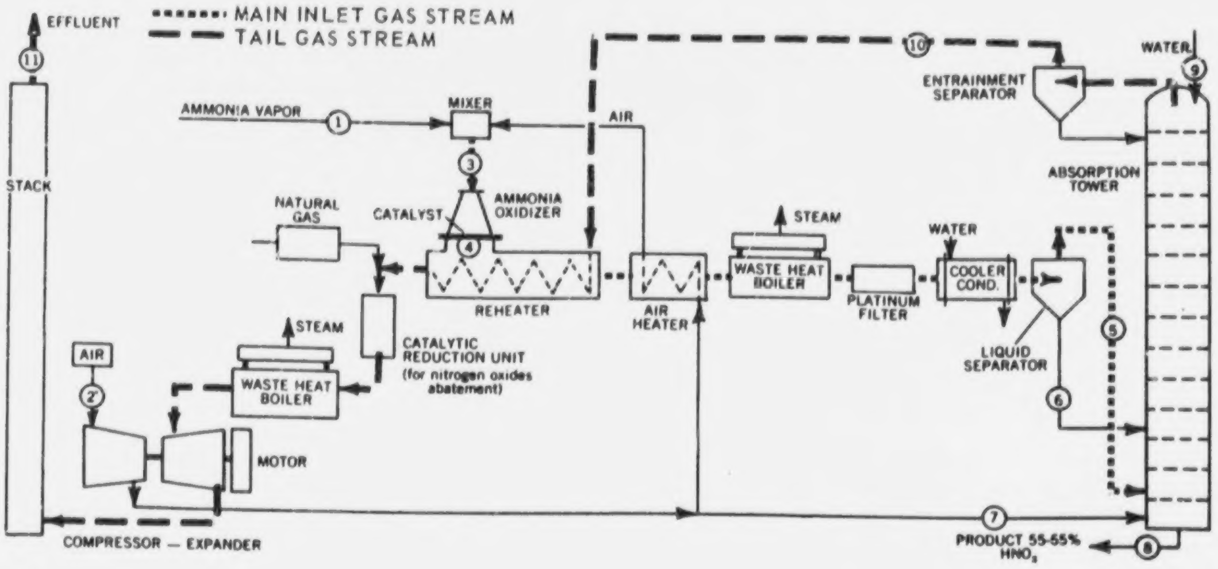

EFFLUENT
MAIN INLET GAS STREAM
TAIL GAS STREAM
11
STACK
AMMONIA VAPOR
1
MIXER
AIR
10
ENTRAINMENT SEPARATOR
WATER
9
3
AMMONIA OXIDIZER
CATALYST
4
NATURAL GAS
REHEATER
AIR HEATER
STEAM
WASTE HEAT BOILER
PLATINUM FILTER
WATER
COOLER COND.
LIQUID SEPARATOR
ABSORPTION TOWER
5
6
STEAM
CATALYTIC REDUCTION UNIT (for nitrogen oxides abatement)
AIR
2
WASTE HEAT BOILER
MOTOR
COMPRESSOR — EXPANDER
7
PRODUCT 55-55% HNO3
8

Figure 7-1. Flow diagram of a typical 120-ton-per-day nitric acid plant utilizing the pressure process.

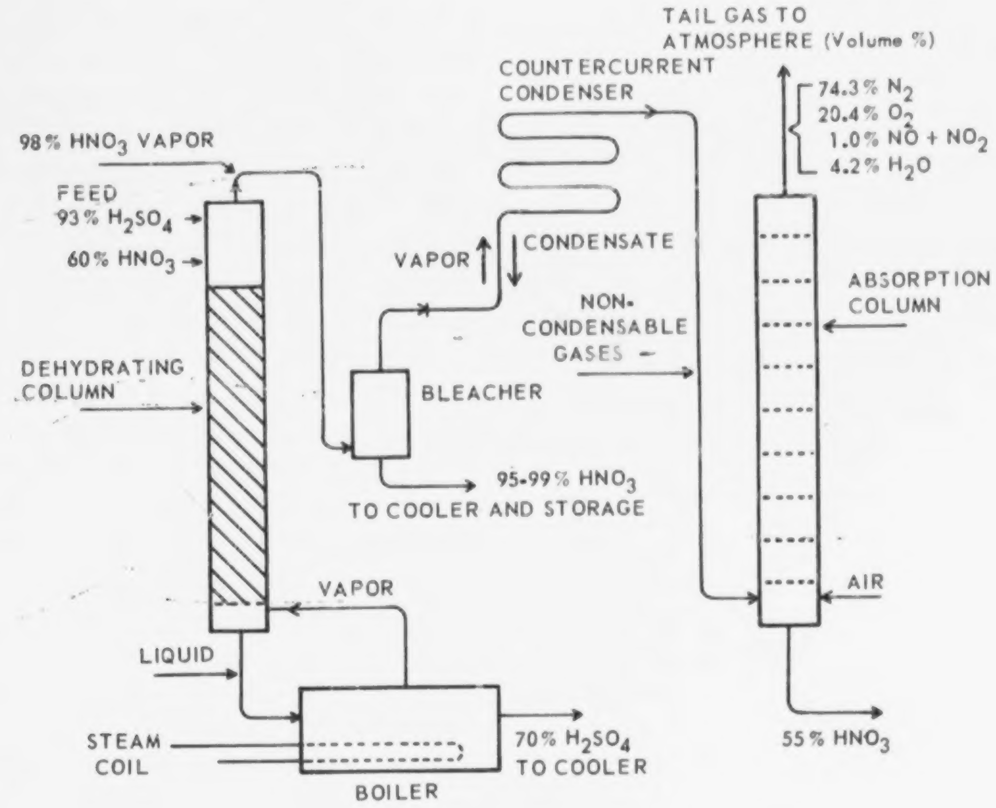

TAIL GAS TO
ATMOSPHERE (Volume %)
74.3% N_2
20.4% O_2
1.0% NO + NO_2
4.2% H_2O
COUNTERCURRENT
CONDENSER
98% HNO_3 VAPOR
FEED
93% H_2SO_4
60% HNO_3
VAPOR
CONDENSATE
NON-
CONDENSABLE
GASES
ABSORPTION
COLUMN
DEHYDRATING
COLUMN
BLEACHER
95-99% HNO_3
TO COOLER AND STORAGE
VAPOR
AIR
LIQUID
STEAM
COIL
70% H_2SO_4
TO COOLER
BOILER
55% HNO_3

Figure 7-2. Nitric acid concentrating unit.

top as a 98 percent nitric acid vapor containing small amounts of NO_X and oxygen, which result from the dissociation of nitric acid. The vapors pass to a bleacher and a condenser to condense nitric acid and separate NO_X and oxygen, which pass to an absorber column for conversion to, and recovery of, nitric acid. Air is admitted to the bottom of the absorber. Dilute sulfuric acid is withdrawn from the bottom of the dehydrating tower and is sent to be concentrated further or be used for other purposes.

The system usually operates at essentially atmospheric pressure.

7.1.1 Emissions

Absorber tail gas is the principal source of NO_X emissions from nitric acid manufacturing. Minor sources are nitric acid concentration and the filling of storage tanks and shipping containers.

Nitrogen oxide emissions from nitric acid manufacturing are estimated at 145,000 tons per year for 1967, about 1 percent of the NO_X from all pollution sources or 2 percent of the pollution from stationary sources. This figure is based on the production of 6.12 million tons of nitric acid in 1967[3] and an average emission factor of 45 pounds NO_X per ton of acid.[2] Without controls, an 800-ton-per-day plant (the largest currently built) would emit about 1,500 pounds of NO_X per hour. Typical tail gas contains about 0.3 volume-percent (300 ppm) of NO_X with about equal concentrations of NO and NO_2.[2] Tail gas is typically reddish-brown or yellow.

In any nitric acid plant, NO_X content of the tail gas is affected by several variables. High levels may be caused by insufficient air supply, high temperatures in the absorber tower, low pressure, producing acid at strengths above design, and internal leaks, which permit gas from ammonia oxidation with high nitrogen oxides content to enter the tail-gas streams. Careful control and good maintenance are required to hold tail-gas nitrogen oxide content to a minimum.

The Hoko process[4] differs from other nitric acid processes by making concentrated

(98 to 99 percent) nitric acid directly. It has found very limited application in the United States, where acid concentrations of 55 to 65 percent are satisfactory for the ammonium nitrate production, which consumes about 75 percent of all nitric acid produced. In the Hoko process, ammonia is combusted with air or oxygen at atmospheric pressure. The combustion gases are cooled to about 30°C, as rapidly as possible, in order to condense and remove water as dilute nitric acid (1 to 2 percent HNO_3). The gas is then compressed, and NO is oxidized to NO_2, which is absorbed in cold concentrated nitric acid. The absorber liquid, an N_2O_4-HNO_3 solution, is mixed with the required volume of water, and the mixture is admitted to an autoclave and oxidized with pure oxygen to make 98 or 99 percent nitric acid. The gas from the absorber is scrubbed with weak acid to remove HNO_3. The NO_x in the tail gas is said to be 0.05 percent by volume.[5] A problem is the disposal of the weak acid formed by condensing the ammonia oxidation vapors.

About 5 pounds of NO_x per ton of nitric acid is emitted in the absorber gas from nitric acid concentration units. Typical NO_x concentration is about 1 percent,[2] reflecting operation at essentially atmospheric pressure. Although figures are not available on the volumes of concentrated nitric acid produced (see Section 7.2), rough estimates of concentrated HNO_3 requirements and resulting NO_x emissions for the United States in 1967 are given in Table 7-1.

Not included in Table 7-1 are acid requirements and NO_x emissions from nitric acid concentration operations for producing military explosives.

7.1.2 Control Techniques

The economic necessity of recovering NO_2 formed in the manufacture and uses of nitric acid has led to a large amount of chemical research that is applicable to problems in NO_x control. It must be recognized, however, that most of this research has been for the recovery of NO_x at around 3,000 ppm; and this is not the same problem as the removal of much lower concentrations of NO_x from stack gases.

A large body of technology has been developed for treating tail gas from nitric acid plants. Catalytic reduction is particularly suited to the nitric acid manufacturing process, and various systems have found wide-spread commercial use. Caustic scrubbing removes NO_x, but there are few commercial applications of this process because of problems in disposing of the spent caustic. Molecular sieve adsorption shows promise and is now offered for commercial use with moisture-free gases.[6,7] Absorption in concentrated sulfuric or nitric acid has been investigated[8] but does not appear competitive.

Table 7-1. ESTIMATES OF STRONG ACID REQUIREMENTS AND NO_x EMISSIONS FROM CONCENTRATION OPERATIONS

Use	Nitric acid requirements			
	Total HNO_3, tons	Strong acid, %	Strong acid, tons/yr	NO_x, tons/yr
Nitrobenzene	90,000	72	65,000	162
Toluene diisocyanate	75,000	51	38,000	95
Commercial explosives	38,000	100	38,000	95
Total	203,000		141,000	352

Catalytic reduction is particularly applicable to the pressure process because the reactor can be placed in the tail gas circuit after the preheater. Energy generated by the reaction of fuel with oxygen and nitrogen oxides is recovered in the turboexpander, increasing power recovery. Thus, the expander may provide most of the power required by the air compressor.[2,9]

Several types of catalytic reduction units have been used with varying degrees of success. All employ fuel to reduce nitrogen oxides, converting NO_2 to NO and NO to N_2. Nonselective reduction uses hydrogen, hydrocarbons, or carbon monoxide[5] as fuel, which reacts with oxygen in the tail gas, as well as with the nitrogen oxides. In selective reduction, ammonia reacts with NO_x in preference to molecular oxygen. In all catalytic reductions, catalyst activity decreases somewhat with use.

Nonselective reduction units include those designed for decolorization and energy recovery, and units designed for NO_x abatement. Decolorization and power recovery units reduce NO_x to NO and burn out part of the oxygen, but their capacity to reduce NO to elemental nitrogen is limited. The purpose of nonselective abatement units is to reduce the NO as well.

In nonselective reduction, the following reactions take place when a preheated mixture of tail gas and methane pass over the catalyst:

$$CH_4 + 4NO_2 \rightarrow 4NO + CO_2 + 2H_2O \quad (4)$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \quad (5)$$

$$CH_4 + 4NO \rightarrow 2N_2 + CO_2 + 2H_2O \quad (6)$$

Similar equations can be written substituting hydrogen for methane; 4 moles of hydrogen is needed to replace 1 mole of methane.

The kinetics are such that reduction reaction (4) is faster than reduction reaction (5), but abatement reaction (6) is much slower than reaction (5). Thus, decolorization can be accomplished by adding just enough fuel for partial oxygen burnout; but if NO_x abatement is required, sufficient fuel must be added for complete oxygen burnout.

Catalytic reduction units for decolorization and power recovery are used in about 50 nitric acid plants in the United States.[10] Many use natural gas for fuel; some use hydrogen. When natural gas is used, tail gas must be preheated to about 900°F to insure ignition. Preheat temperatures as low as 300°F will insure ignition with hydrogen.[5]

Catalytic reduction is highly exothermic. The temperature rise for the reaction with methane is about 230°F for each percent oxygen burnout, and with hydrogen it is about 270°F.[2] For decolorization, the outlet temperature is ordinarily limited to 1200°F, the maximum temperature limit of turboexpanders with current technology.[10] Increased power recovery may justify adding sufficient methane to reach the temperature limit of the turbine.

Supported platinum or palladium catalysts are employed in decolorization. Catalyst supports include ceramic spheres, ceramic pellets, ceramic honeycomb, and woven nickel-chromium ribbon. The honeycomb structure is reported to give low pressure drop at the high space velocities of 100,000 volumes per hour per volume. In new decolorization units, honeycomb supports are favored over ceramic spheres and pellets, which require lower hourly space velocities of 30,000 volumes per hour per volume.[11-13]

At a given level of NO_2 removal, the nickel-chromium-supported catalyst uses more fuel, but is said to convert more NO to N_2 than the ceramic supported catalyst.[10]

Both catalyst and nitric acid manufacturers report satisfactory performance for decolorization units. The reduction of total NO_x is limited, but ground-level NO_2 concentration in critical areas near the plant is reduced substantially.[10]

Nonselective catalytic abatement is more difficult technically than decolorization, and commercial results have been less satisfactory. Provisions must be made to control the heat released in burning out all the oxygen from the tail gas, which must be done before extensive NO reduction proceeds.

As mentioned above, tail gas must be preheated to 900°F to insure ignition when methane is used as the reducing agent. Outlet temperatures would reach 1,370° and 1,590°F for 2 and 3 percent oxygen burnout, respectively. These temperatures compare to the 1,200°F maximum temperature limit for current turboexpanders and the 1,500° to 1,600°F maximum limit for catalyst. For single-stage operation, the oxygen in the tail gas cannot exceed 2.6 percent to remain within the temperature limit of the catalyst, and cooling must be provided to meet the turboexpander limit. Older turbines may have even lower temperature limitations.

Two or three plants are known to have installed single-space nonselective abaters. They are believed to have been designed for natural gas.[10] As noted above, oxygen concentration cannot exceed about 2.6 percent. The reactors must be designed to withstand 1,500° to 1,550°F at 100 to 120 psig, which requires costly refractories or alloys. Ceramic spheres are used as catalyst supports, at hourly gas space velocities up to 30,000 volumes per hour per volume.[10] One company reports that they have been able to maintain NO_x levels of 500 ppm or less over an extended period of time. Operation close to 300 ppm might be obtained. Catalyst suppliers report values of 100 ppm from small-scale tests with gas of fixed composition. On a plant scale, the effluent gas must be cooled by heat exchange or quench to meet the temperature limitation of the turbine. It would be logical to use a waste heat boiler to generate steam.

A somewhat cheaper but less successful alternative is two-stage reduction for abatement. Two or three commercial installations are known in the United States. One system involves two reactor stages with interstage heat removal.[13] Another two-stage system for abatement involves preheating 70 percent of the feed to 900°F, adding fuel, and passing the mixture over the first-stage catalyst. The fuel addition to the first stage is adjusted to obtain the desired outlet temperature. The remaining 30 percent of the tail gas, preheated to only 250°F, is used to quench the first-stage effluent. The two streams plus the fuel for complete reduction are mixed and passed over the second-stage catalyst; the effluent passes directly to the turboexpander. This system avoids high temperatures, and the use of coolers and waste heat boilers.[5,14,15]

Honeycomb ceramic catalysts have been employed in two-stage abatement, with hourly gas-space velocities of about 100,000 volumes per hour per volume in each stage.[12]

Commercial experience with single-stage catalytic abaters has been modestly satisfactory, but two-stage units operating on natural gas have not been as successful. Two-stage units designed for abatement have frequently achieved abatement for periods of only a few weeks, at which point declining catalyst activity results in increasing NO levels. Recent data indicate that successful abatement can be maintained for somewhat longer periods. Units that no longer abate NO emissions can, however, continue to serve for energy recovery and decolorization.[10]

The success of single-stage abaters compared to the limited success of two-stage units may result from the following factors: the catalyst is in a reducing atmosphere; the temperatures are higher; and spherical rather than honeycomb catalyst supports are used. It has not been practical to change catalyst type in two-stage units because the reactors designed for a space velocity of 100,000 volumes per hour per volume would be too small to accommodate a spherical catalyst, which effectively removes NO at a space velocity of about 30,000. The failure of the honeycomb catalyst in NO reduction compared to its success in decolorization may reflect that reaction kinetics make it much more difficult to reduce NO than NO_2.[10]

Fuel requirements are 10 to 20 percent over stoichiometric for nonselective abatement with methane. Some hydrocarbons and CO appear in treated tail gas. Furthermore, not all methane is converted in decolorization. Less surplus fuel is required when hydrogen is used.[10]

Selective catalyst abatement must be carried out within the narrow temperature range of 410° to 520°F. Within these limits, ammonia will reduce NO_2 and NO to molecular nitrogen, without simultaneously reacting with oxygen. The reactions are shown in the following equations:

$$8NH_3 + 6NO_2 \rightarrow 7N_2 + 12H_2O \quad (7)$$

$$4NH_3 + 6NO \rightarrow 5N_2 + 6H_2O \quad (8)$$

Above 520°F, ammonia may oxidize to form NO_x; below 410°F, it may form ammonium nitrate.[2]

Three commercial plants have installed selective abatement units. Performance to date has ranged from unsatisfactory to partly successful. The reaction supplies little energy for recovery in the turboexpander.[10]

A number of World War II vintage nitric acid plants of 55 tons per day capacity are equipped with reciprocating compressors for power recovery. If selective abaters were installed in front of their expanders, ammonium salts could enter the lubricating oil system, and an explosion could result. This is not a problem with turboexpanders.

Platinum on a honeycomb support is used in selective abatement. This catalyst system has not been very successful up to the present time; consequently, nitric acid manufacturers do not consider selective abatement to be commercially developed yet.[10] Platinum on pellets may be satisfactory for this service.[12] The very high cost of platinum catalysts and the necessity of using them only on a gas stream that is essentially free of sulfur compounds limit the number of analogous stack gases with which they can be used.

Caustic scrubbing is an alternative method of removing NO_x from nitric acid tail gas. Sodium hydroxide, sodium carbonate, ammonium hydroxide, and calcium carbonate react with NO_x to form nitrite and nitrate salts. Examples of 90 percent removal of NO_x by caustic scrubbing have been reported in the literature.[16] The high removal levels probably reflect a favorable NO/NO_2 ratio of about 1:1.

Although sodium hydroxide or sodium carbonate scrubbing removes NO_x from tail gas, it has not found extensive use in the industry because of the difficulties encountered in disposing of the spent solution; the nitrite and nitrate salts contained in the spent solution become a serious water pollutant if released as a liquid effluent. The concentrations are too dilute for economic recovery of the salts.[10]

Several potential processes for tail gas treatment are still to be tested commercially. Molecular sieves have been reported to be much more effective adsorbents for NO_x in tail gas than silica gel.[6,7] They have recently become commercially available for this purpose, and limited evidence indicates that they work well. The adsorbed NO_x can be desorbed as enriched NO_x or HNO_3 by displacement with hot air or steam, and returned to the nitric acid plant. Silica gel is probably more acid resistant than the zeolites.

NO_x can be adsorbed in nitric acid or sulfuric acid. Sulfuric acid readily absorbs a 50/50 mixture of NO/NO_2. The tail gas also contains water, which would dilute the sulfuric acid. Reconcentration makes sulfuric acid absorption costly.

Concentrated nitric acid would be expected to absorb some NO as well as the 50/50 mixture of NO/NO_2. Again, the abundance of water in tail gas would dilute the acid. Absorption of NO_x from tail gas by 20 to 35 percent HNO_3, followed by regeneration of the contaminated acid with oxygen, has been proposed in the literature.[8]

Emissions from storage tanks can be collected through a vapor recovery system and returned to the process feed, as can emissions from nitric acid concentration. The equipment should be constructed of stainless steel. Frequently, emissions from this source are disposed of by incineration, which reduces the NO_X content by 75 to 90 percent.[17] Nitrogen oxide incineration is covered in Section 7.2.3.2.

7.1.3 Costs for Control

By careful design and operation, some nitric acid manufacturers attain NO_X levels in untreated tail gas of 0.1 to 0.2 percent versus a typical level of 0.3 percent.[10] The optimum level of NO_X in tail gas depends on the economic factors prevailing at each location: 0.1 percent reduction in NO_X means approximately 1 percent improvement in nitric acid recovery. The difference between the credits for improved recovery and the added cost for additional absorber stages, increased cooling, etc., determines the optimum level. If abatement is required, its costs enter into the economic calculations.

Costs of emission controls may be partially offset by credits for products or energy recovery. If NO_X can be removed from tail gas and recovered at a high concentration, it may be returned as feed to the process. The value of the recovered NO_X is a potential credit for developing an adsorption process. On the other hand, the cost of recovering dilute nitrite and nitrate salts in spent caustic may outweigh their product value. In catalytic reduction, all the products are released to the atmosphere, but the energy released in the reaction may be economically recovered in a turboexpander or waste heat boiler.

Costs for catalytic reduction will be affected by the type of treatment (nonselective decolorization of abatement, selective abatement, etc.), the volume of tail gas to be treated, the cost of fuel, and the value of the energy recovered.

Adding catalytic reduction capabilities to an existing unit is usually more difficult and costly than incorporating the facilities into a new unit as it is being designed. For existing plants, modifications to the heat exchanger train may be required to obtain and hold tail-gas temperatures within the operable range. Physical space limitations may preclude placing the reactor ahead of the turboexpander. Additional preheat facilities would be required in placing the reactor after the turboexpander, and energy generated in the reduction would not be available for recovery in the turboexpander. For these reasons, costs of adding catalytic reduction equipment to existing plants will vary with each application and will depend upon the modifications required for the installation.

Rough costs of three catalytic reduction alternatives have been derived during the planning of a new 300-ton-per-day nitric acid plant. These alternatives are (1) decolorization, (2) single-stage selective abatement, and (3) two-stage nonselective abatement. The comparison is shown in Table 7-2. The costs are strongly affected by conditions specific to the location and should not be used for other locations.

In this comparison, investments for the abatement systems are two to four times the investment for decolorization. Selective abatement requires less investment than two-stage abatement. Overall operating costs, including a 20 percent return before income taxes, are approximately breakeven for decolorization. For most companies, this corresponds to an after-tax return of 10 percent, which is the current cost of capital. Operating costs for two-stage abatement are lower than for nonselective abatement, since steam credits more than offset higher investment and fuel costs.

In this plant, a turboexpander augmented by a steam turbine drives the compressor supplying air for the oxidation of ammonia. Without catalytic reduction, tail gas would be preheated by exchange to a temperature 140°F below the limit for the turboexpander. In the decolorization alternative, fuel addition rate is set so that the heat release meets the temperature limit of the turboexpander. The additional power recovery at the expander is balanced by reducing steam to the turbine. In selective abatement, steam savings are smaller because the selective reduction provided only a 60°F temperature rise. In two-stage, nonselective abatement, additional steam savings are obtained by placing a waste heat boiler between stages, since only 140° of the 680°F

Table 7-2. ESTIMATED COSTS OF CATALYTIC REDUCTION FOR THREE CONTROL SYSTEMS

	Decolorizer	Selective abater	Two-stage non-selective abater
NO_x before reduction, ppm	3000	3000	3000
NO_x after reduction, ppm	3000	300	300
Fuel	Natural gas	Ammonia	Natural gas
Investment, 10^3 \$	60	140	255
\$/scfm	2.60	6.10	11.00
Costs, 10^3 \$/yr[a]			
Natural gas	14	--	82
Ammonia	--	33	--
Catalyst	4	12	8
Steam	(50)	(21)	(144)
Investment-based costs[b]	30	70	128
Total cost, 10^3 \$/yr	(2)	94	74
Total cost, \$/ton HNO_3	(0.02)	0.95	0.75
Total cost, \$/ton NO_x removed	--	34	27

[a] Parentheses indicate negative costs or savings.

[b] Includes 20 percent return before taxes.

total temperature rise can be used in the turboexpander.

Investment-based costs are assumed at 50 percent per annum, including a 20 percent return before income tax. Steam is credited at 75¢ per thousand pounds; natural gas is charged at 40¢ per 1,000 Btu; and ammonia, at $50 per ton. Catalytic life was assumed to be 6 years for nonselective operation and 2 years for selective.

To the extent that abatement is not yet completely satisfactory, the basis for this study has not been completely demonstrated.

In the mid-1950's, a catalytic decolorizer was installed on a high-pressure-type nitric acid plant somewhat smaller than those referred to in Table 7-2, at a cost of $50,000. A recent estimate for a catalytic control device for a low-pressure nitric acid plant of somewhat greater capacity than the plants in Table 7-2 was $400,000. This was to be a unit for decolorization or one-step, nonselective abatement, the choice depending upon the amount of synthesis gas ($3N_2 + H_2$) mixed with the tail gas. Operating costs per ton of nitric acid was estimated at $0.90 for decolorization and $2.30 for abatement.[18]

Investments for catalytic reduction must provide for catalyst, reactor vessel, controls, and heat-exchange equipment. Honeycomb catalyst costs about $2,000 per cubic foot whereas spherical catalysts cost about $700 per cubic foot.[10] The costs per scfm of tail gas are about equal, however, because honeycomb systems are designed for 100,000 standard cubic feet per hour (scfh) of gas per cubic foot of catalyst, while spherical catalyst systems are designed for space velocities of about 30,000 scfh of gas per cubic foot of catalyst. Thus, catalyst investments are about $1.20

per scfm of tail gas or $100 per ton per day of nitric acid. If two catalyst stages are employed, the investment must be doubled.

Heat-exchanger investments range widely from a low of zero for equipping some new plants with decolorizers to about $85,000 for a waste-heat-boiler system in a 300-ton-per-day nitric acid plant in a single-stage abater and perhaps higher costs for two-staged units.

A complete design and equipment list is needed to obtain costs for any specific plant. In general, unit investment per pound per day of NO_x removal varies inversely with plant size; the small plant is, therefore, at a cost disadvantage relative to the large plant.

Operating costs must cover the cost of fuel, repair labor and materials, catalyst replacement, and capital charges. Fuel costs are dependent on location and vary with the type of fuel burned. Usually natural gas is less expensive than hydrogen because, though costs per 1,000 scf are about the same, only 25 percent as much is required. Hydrogen costs may approach the cost of methane when waste hydrogen is available, but the amount available from ammonia manufacture would usually be adequate only for decolorization, and the supply would not be available during the ammonia plant shutdowns.

Costs were not developed for caustic scrubbing because disposal of spent caustic solution prohibits use of this method at most locations. An estimate of the cost of adding a two-stage abater to an existing plant has been given by Decker[13] as ranging from about $750 to $1125 per ton per day of nitric acid capacity for abatement corresponding to that shown in Table 7-2. The abater is installed after the turbine; thus, there is no credit for energy recovery. This operation is said to require fuel costs of 50c per ton of HNO_3.

7.2 NITRIC ACID USES

Important uses of nitric acid and the estimated quantities consumed in each use are listed in Table 7-3. The basis for these estimates is given in the corresponding section below.

Approximately 75 percent of the nitric acid produced in the United States is consumed in making ammonium nitrate; adipic acid manufacture consumes about 9 percent. No other single outlet consumes more than about 4 percent. Other uses include metal pickling and etching, nitrations and oxidations of organic compounds, and production of metallic nitrates.

Table 7-3. ESTIMATED NITRIC ACID CONSUMPTION IN UNITED STATES, 1967

Use	Quantity, tons
Ammonium nitrate	4,540,000
Adipic acid	560,000
Terephthalic acid	100,000
Nitrobenzene	90,000
Toluene diisocyanate	75,000
Commercial explosives (e.g., NH_4NO_3)	38,000
Fertilizers (e.g., NH_4NO_3)	150,000
Other uses	569,000
Total	6,122,000[19]

7.2.1 Ammonium Nitrate Manufacture

Ammonium nitrate is produced by the direct neutralization of nitric acid with ammonia:

$$NH_3 + HNO_3 \rightarrow NH_4NO_3$$

About 0.81 ton of nitric acid (100 percent equivalent) and 0.210 to 0.225 ton of anhydrous ammonia are required to make 1 ton of ammonium nitrate. In actual practice 100 percent nitric acid is not used, and typical feed acid contains 55 to 60 percent HNO_3. The product is an aqueous solution of ammonium nitrate, which may be used as liquid fertilizer or converted into a solid product. The strength of the solution varies. The heat of reaction is usually used to evaporate part of the water, giving typically a solution of 83 to 86 percent ammonium nitrate. Further evaporation to a solid may be accomplished in a falling-film evaporator,[20] in a disk-spraying plant,[21] or by evaporation to dryness in a raked shallow open pan (graining).[21]

Much of the solid ammonium nitrate produced in the United States is formed by "prilling," a process in which molten ammonium nitrate flows in droplets from the top of a tower countercurrent to a rising stream of air, which cools and solidifies the melt to produce pellets or prills.[22]

In 1967, 5.606×10^6 tons of ammonium nitrate was produced.[19] At a nitric acid consumption rate of 0.81 ton per ton of ammonium nitrate, this production required about 4.54×10^6 tons of nitric acid. About 0.7×10^6 to 0.8×10^6 tons[23] was used in explosives, and most of the remainder was used in direct application or in mixed fertilizers.

7.2.1.1 Emissions

No significant amount of NO_x is produced in this process; the most likely source of nitric acid emissions would be the neutralizer. The vapor pressure of ammonia, however, is much higher than the vapor pressure of nitric acid, and the release of nitric acid fumes or NO_x is believed to be negligible,[24] especially since a slight excess of NH_3 is used to reduce product decomposition.

Because NO_x emission is negligible, no controls are required.

7.2.2 Organic Oxidations

Nitric acid is used as an oxidizing agent in the commercial preparation of adipic acid, terephthalic acid, and other organic compounds containing oxygen. The effective reagent is probably NO_2, which has very strong oxidizing power.

Adipic acid, $COOH \cdot (CH_2)_4 \cdot COOH$, is a dibasic acid used in the manufacture of synthetic fibers. In the United States, adipic acid is made in a two-step operation as shown in Figure 7-3.

The first step is the catalytic oxidation of cyclohexane by air to a mixture of cyclohexanol and cyclohexanone. In the second step, adipic acid is made by the catalytic oxidation of the cyclohexanol/cyclohexanone mixture using 45 to 55 percent nitric acid. The product is purified by crystallization.[25] The whole operation is continuous.

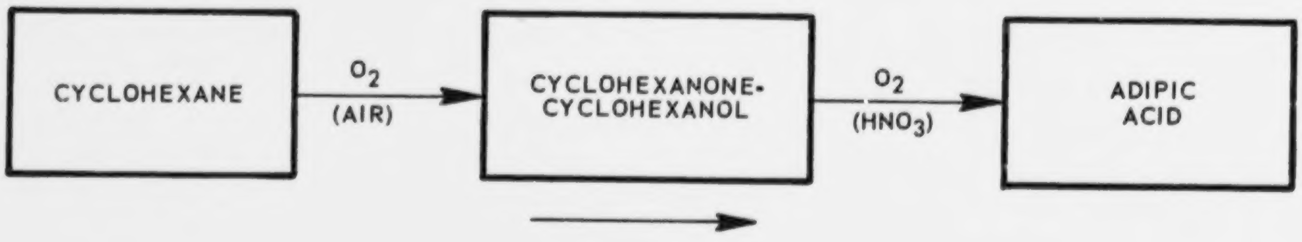


Figure 7-3. Adipic acid synthesis.

In oxidizing cyclohexanol/cyclohexanone, nitric acid is reduced to unrecoverable N_2O and potentially recoverable NO and NO_2. According to Lindsay,[26] the nitric acid requirement is 1.46 pounds per pound of chemically formed adipic acid, of which 0.43 pound is potentially recoverable NO_x and 1.03 pounds is unrecoverable N_2O.

Terephthalic acid is an intermediate in the production of polyethylene terephthalate, which is used in polyester, films, and other miscellaneous products. Some terephthalic acid can be produced in various ways, one of which is by the oxidation of paraxylene by nitric acid. The nitric acid oxidation proceeds in two steps as shown in Figure 7-4. Both steps take place in a single reactor. The first step yields primarily N_2O, while the second step yields mostly NO in the offgas.[27] Based on this information, the nitric acid requirement for terephthalic acid is estimated to be 1.33 pounds per pound of terephthalic acid, of which 0.76 pound is potentially recoverable (NO) and 0.57 pound is unrecoverable (N_2O).

In 1967, total estimated terephthalic acid production was about 395,000 tons, an estimated 150,000 tons of which was made via nitric acid oxidation. Estimated adipic acid production was about 540,000 tons,[28] all of which is believed to be made from the nitric acid oxidation of cyclohexanol/cyclohexanone. Nitric acid is used for the oxidation of other organic compounds in addition to terephthalic acid and adipic acid, but none is believed to approach these two in product volume.

7.2.2.1 Emissions

No data are available on NO_x emissions released to the atmosphere from manufacturing operations using nitric acid as an agent for oxidizing organic compounds. The offgases leaving the reactor after nitric acid oxidation of organic materials may contain as much as 50 percent NO_x before processing for acid recovery.[26,27] N_2O, one of the principal compounds of the offgas, is not counted as NO_x, since it is not oxidized to NO_x in the atmosphere and is considered harmless.

NO_x emissions and nitric acid requirements were roughly estimated, based on references 26 and 27, by assuming that NO_x in adsorber offgas would be reduced to 0.3 percent, a level typical or nitric acid plants. The absorption systems recover an estimated 98 to 99 percent of the NO_x as nitric acid and recycle it back to the unit. The rough estimates are shown in Table 7-4.

The estimated NO_x emissions from these two sources amount to 0.05 percent of total NO_x emissions from all stationary sources, or 0.03 percent of total NO_x emissions from all sources in the United States.

7.2.2.2 Control Techniques

In commercial operations, economy requires the recovery of NO_x as nitric acid. It is recovered by mixing the offgas with air and sending the stream to an absorbing tower, where nitric acid is recovered as the stream descends and unrecoverable N_2O and nitrogen pass off overhead. The recovery process is similar to the NO oxidation described in Section 5; the system is similar to the absorption sections of a nitric acid plant, as described in the same section.

Should the resulting emission rates be considered too high, further reduction could be attempted by standard techniques such as incineration in a reducing flame or additional absorption (Section 4.3).

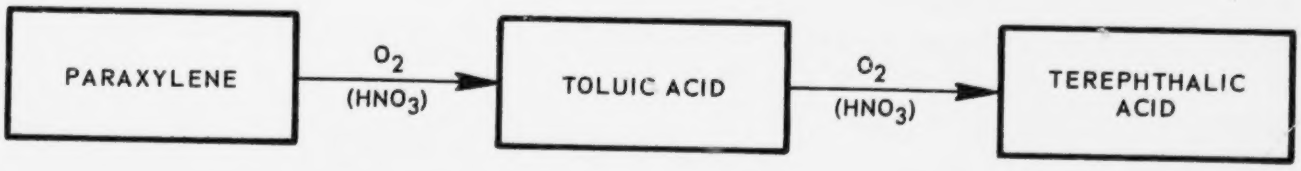


Figure 7-4. Terephthalic acid synthesis.

Table 7-4. ESTIMATED ACID REQUIREMENTS AND NO_x EMISSIONS FROM NITRIC ACID OXIDATION OF ORGANIC COMPOUNDS, 1967

	Adipic acid	Terephthalic acid
Production rate,[28] 10^6 lb/yr	1,080.00	300.00[a]
Net HNO_3 consumption,[b] lb/lb product	1.04	0.68
Net HNO_3 consumption,[b] tons/yr	560,000.00	100,000.00
NO_x emissions, lb/ton product	11.60	13.00
NO_x emissions, tons/yr	3,000.00	1,000.00

[a] Terephthalic acid produced by nitric acid oxidation only.

[b] After crediting for HNO_3 recovered from offgases.

A potential, long-range control for eliminating NO_x from organic oxidation processing is the replacement of nitric acid as an oxidant by catalytic processes using air or oxygen. Most terephthalic acid is now produced via catalytic processes using air oxidation. The laboratory catalytic oxidation of cyclohexanol and cyclohexanone by air to adipic acid has also been reported,[29] but no commercial process is known.

7.2.2.3 Costs of Control

Economy requires that nitric acid be recovered from reactor offgas in large-scale organic oxidations using nitric acid as the oxidizing agent. For example, the incentive for acid recovery for a 100-million-pound-per-year adipic acid plant would be about $1.6 million per year. This figure is based on recovering 0.3 pound of HNO_3 per pound of adipic acid at a nitric acid cost of $3.90 per 100 pounds.[30] The optimum economic recovery level depends upon economic factors at each installation.

7.2.3 **Organic Nitrations**

Nitration is the treating of organic compounds with nitric acid (or NO_2) to produce nitro compounds or nitrates. The following equations illustrate the two most common types of reaction:

$$RH + HONO_2 \rightarrow RNO_2 + H_2O \quad (1)$$

$$ROH + HONO_2 \rightarrow RONO_2 + H_2O \quad (2)$$

Examples of products of the first reaction (C-nitration) are compounds such as nitrobenzene, nitrotoluenes, and nitromethane. Nitroglycerin (or glyceryl trinitrate) and nitrocellulose are examples of compounds produced by the second reaction (O-nitration).

Nitrating agents used commercially include nitric acid, mixed nitric and sulfuric acids (mixed acids), and NO_2. Mixed nitric and sulfuric acid is most frequently used. The sulfuric acid functions to promote formation of NO_2^+ ions and to absorb the water produced in the reaction.

Nitrations are carried out in either batch or continuous processes. The trend is toward continuous processes, since control is more easily maintained, equipment is smaller, system holdup is smaller, and hazards are reduced. A multiplicity of specialty products such as dyes and drugs, which are produced in small volumes, will continue, however, to be manufactured by small batch nitrations.

Batch nitration reactors are usually covered vessels provided with stirring facilities and cooling coils or jackets. The reactor bottom is sloped, and product is withdrawn from the lowest point. When products are potentially explosive, a large tank containing water (drowning tank) is provided so that the reactor contents can be discharged promptly and "drowned" in case of abnormal conditions.

When the reaction is completed, the reactor contents are transferred to a separator, where the product is separated from the spent acid. The product is washed, neutralized, and purified; spent acids are processed for recovery. Figure 7-5 illustrates a batch nitration process for manufacturing nitroglycerin.[31]

Continuous nitration for nitroglycerin is carried out in many types of equipment. Two widely employed processes are the Schmid-Meissner process (illustrated in Figure 7-6) and the Biazzi process (illustrated in Figure 7-7).[31] Both processes provide for continuous reaction, separation, water washing, neutralization, and purification. The Biazzi process makes greater use of impellers for contacting than the Schmid-Meissner, which uses compressed air to provide agitation during washing and neutralizing. Both types of equipment can be used for nitrating in general.

When mixed acid is used, the spent acid is recovered in a system similar to that shown in Figure 7-8.[31] The mixed acid enters the top of the denitrating tower. Superheated steam is admitted at the bottom to drive off the spent nitric acid and NO_x overhead. The gases are passed through a condenser to liquefy nitric acid, which is withdrawn to storage; the uncondensed gases are then sent to an absorption tower. Weak sulfuric acid is withdrawn from the bottom of the denitrator tower and concentrated or disposed of by some convenient arrangement.

When nitric acid alone is used for nitration, the weak spent acid is normally recovered by sending it to an absorption tower, where it replaces some of the water normally fed as absorbent.

Nitrobenzene and dinitrotoluenes are produced in large volumes as chemical intermediates. Explosives such as TNT, nitroglycerin, and nitrocellulose are produced in significant but lesser volumes.

Nitrobenzene is manufactured in both continuous and batch nitration plants. Mixed acids containing 53 to 60 percent H_2SO_4, 32 to 39 percent HNO_3, and 8 percent water are used in batch operations, which may process 1,000 to 1,500 gallons of benzene in 2 to 4 hours. Continuous plants, as typified by the Biazzi units (Figure 7-7) also use mixed acids. A 30-gallon continuous nitrator has the capacity of a 1,500-gallon batch nitrator. Yields are 95 to 99 percent of theoretical.[32]

The major use of nitrobenzene is in the manufacture of aniline. It is also used as a solvent. Nitrobenzene production in 1967 was an estimated 170,000 tons. Nitric acid requirements are approximately 0.53 pound per pound of nitrobenzene.[32] On this basis, nitric acid used in nitrobenzene synthesis was estimated at 90,000 tons for 1967.

Dinitrotoluene is manufactured in two stages in both continuous and batch units. The first stage is the nitration of toluene to mononitrotoluene, which is nitrated to dinitrotoluene in the second stage. For making mononitrotoluene in the batch process, mixed acid consisting of 28 to 32 percent HNO_3, 52 to 56 percent H_2SO_4, and 12 to 20 percent water is used in equipment sized to handle up to 3,000 gallons. Operating temperature ranges from 25° to 40°C. Mononitrotoluene yields of 96 percent are typical.[33]

The second step, the production of dinitrotoluene, is carried out separately because it requires more severe conditions.

Dinitrotoluene is made from mononitrotoluene using stronger mixed acid containing 28 to 34 percent HNO_3, 60 to 64 percent H_2SO_4, and 5 to 8 percent water. Temperatures are increased to 90° C after all the acid has been added. Dinitrotoluene yields are about 96 percent of theoretical.[33]

The principal use of dinitrotoluene is as an intermediate in making toluene diisocyanate (TDI) for use in polyurethane plastics. It is usually supplied as mixtures of the 2,4 and 2,6 isomers. In 1967, about 200 million pounds of toluene diisocyanate was produced, which required 75,000 tons of nitric acid, estimated on the basis of 0.74 pound of nitric acid per pound of TDI.

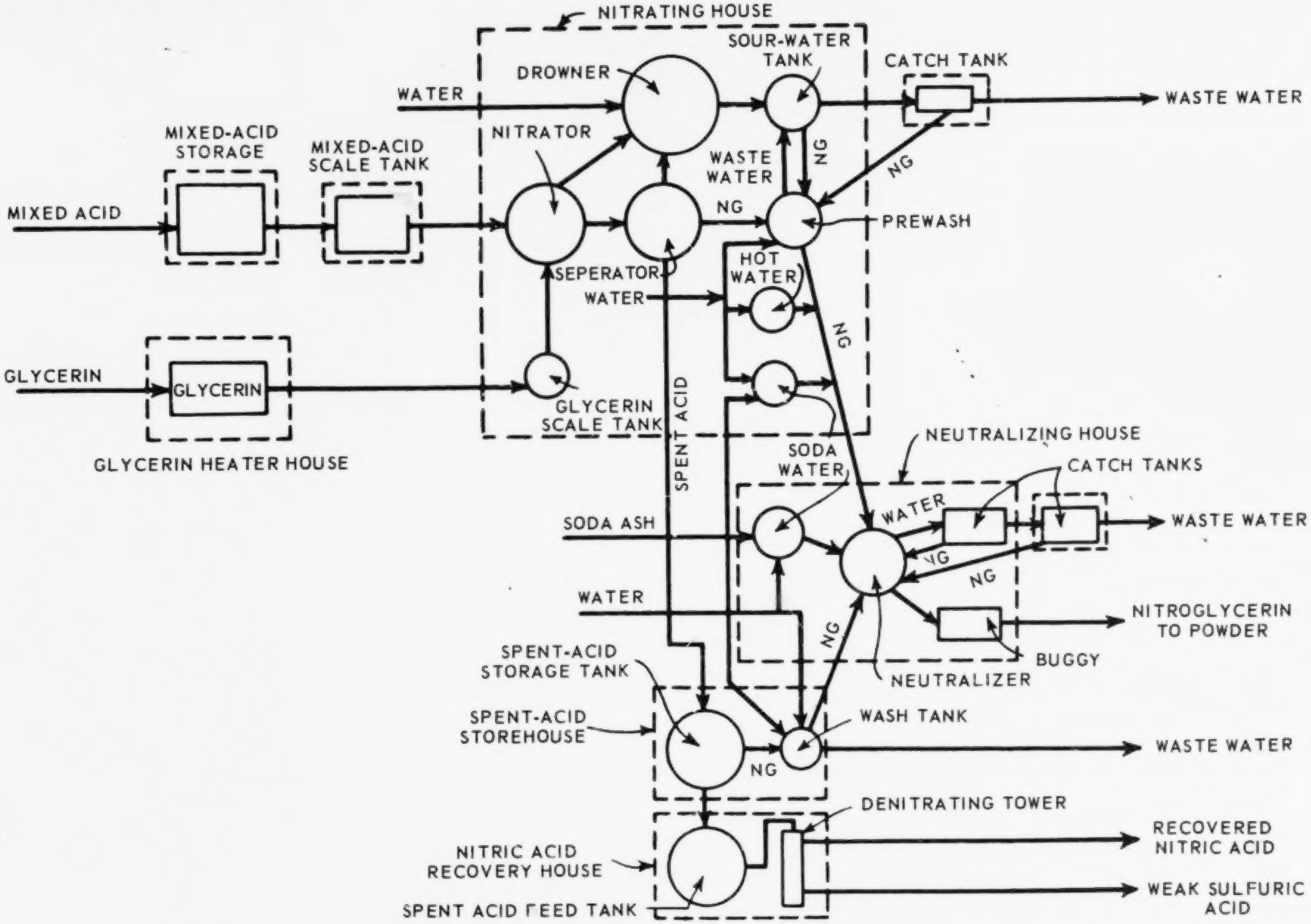

NITRATING HOUSE
DROWNER
SOUR-WATER TANK
CATCH TANK
WASTE WATER
WATER
NITRATOR
MIXED-ACID STORAGE
MIXED-ACID SCALE TANK
WASTE WATER
NG
NG
MIXED ACID
NG
PREWASH
SEPERATOR
HOT WATER
WATER
NG
GLYCERIN
GLYCERIN
GLYCERIN SCALE TANK
SPENT ACID
GLYCERIN HEATER HOUSE
SODA WATER
NEUTRALIZING HOUSE
CATCH TANKS
SODA ASH
WATER
WASTE WATER
NG
NG
WATER
NITROGLYCERIN TO POWDER
NG
BUGGY
SPENT-ACID STORAGE TANK
NEUTRALIZER
SPENT-ACID STOREHOUSE
WASH TANK
WASTE WATER
NG
DENITRATING TOWER
NITRIC ACID RECOVERY HOUSE
RECOVERED NITRIC ACID
WEAK SULFURIC ACID
SPENT ACID FEED TANK

Figure 7-5. Batch process for the manufacture of nitroglycerin (NG).[31]

(Courtesy of John Wiley and Sons, Inc.)

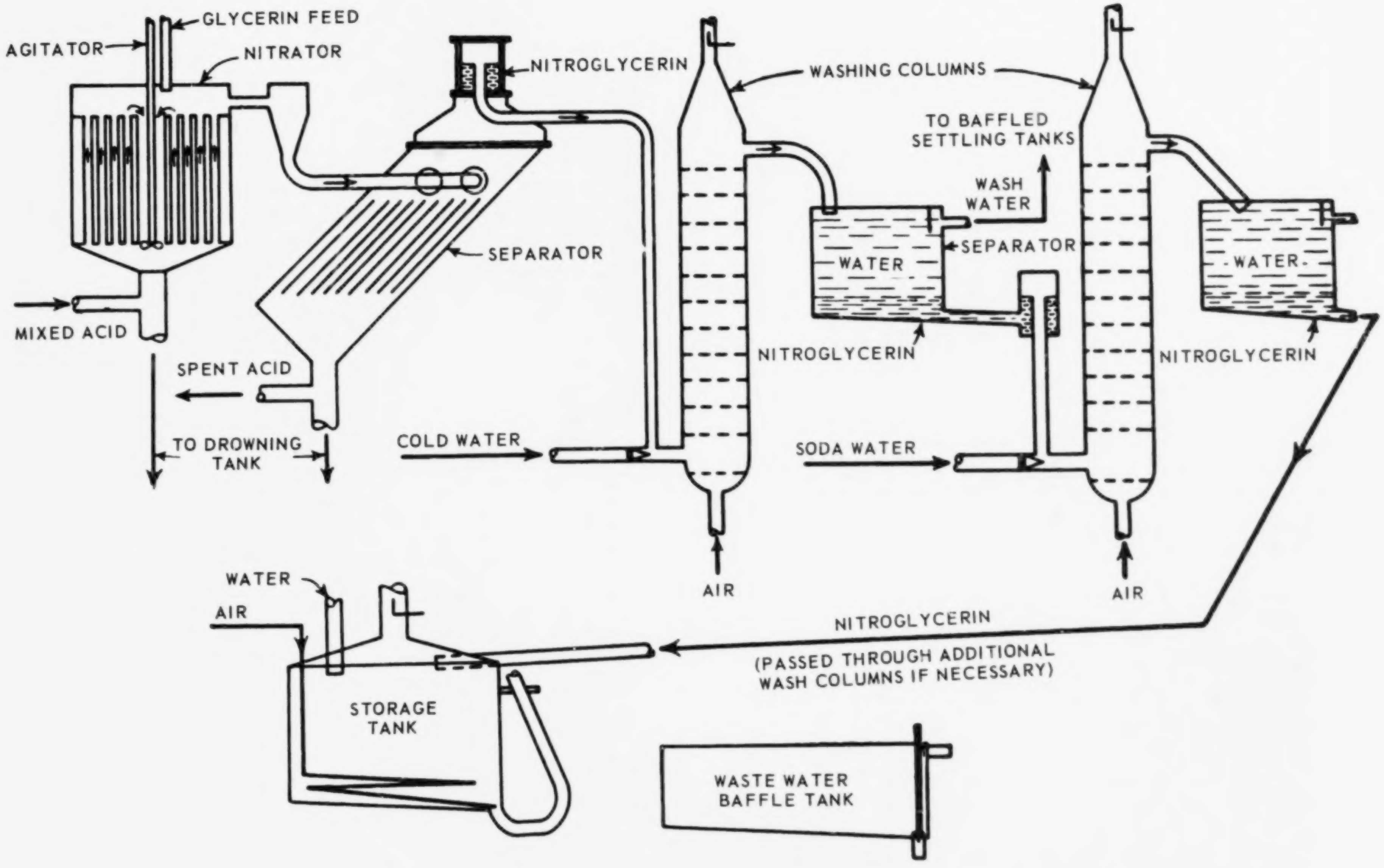

GLYCERIN FEED
AGITATOR
NITRATOR
MIXED ACID
SPENT ACID
TO DROWNING TANK
NITROGLYCERIN
SEPARATOR
COLD WATER
WASHING COLUMNS
TO BAFFLED SETTLING TANKS
WASH WATER
SEPARATOR
WATER
NITROGLYCERIN
SODA WATER
WATER
NITROGLYCERIN
AIR
AIR
WATER
AIR
NITROGLYCERIN
(PASSED THROUGH ADDITIONAL WASH COLUMNS IF NECESSARY)
STORAGE TANK
WASTE WATER BAFFLE TANK

Figure 7-6. Schmid-Meissner continuous-nitration plant.[31]
(Courtesy of John Wiley and Sons, Inc.)

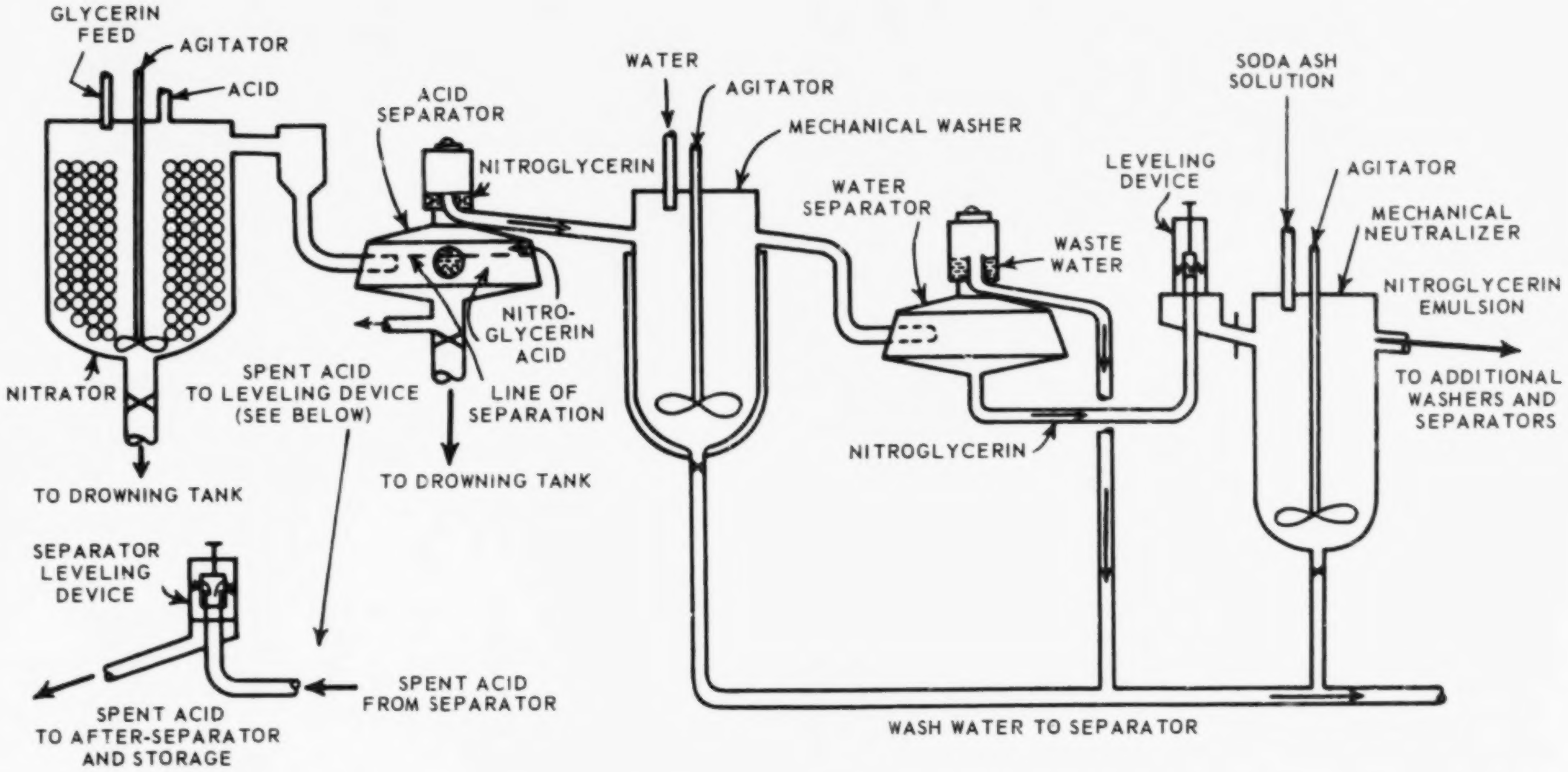

GLYCERIN FEED
AGITATOR
ACID
NITRATOR
TO DROWNING TANK
ACID SEPARATOR
NITROGLYCERIN
NITRO-GLYCERIN ACID
LINE OF SEPARATION
SPENT ACID TO LEVELING DEVICE (SEE BELOW)
TO DROWNING TANK
SEPARATOR LEVELING DEVICE
SPENT ACID TO AFTER-SEPARATOR AND STORAGE
SPENT ACID FROM SEPARATOR
WATER
AGITATOR
MECHANICAL WASHER
WATER SEPARATOR
WASTE WATER
NITROGLYCERIN
LEVELING DEVICE
SODA ASH SOLUTION
AGITATOR
MECHANICAL NEUTRALIZER
NITROGLYCERIN EMULSION
TO ADDITIONAL WASHERS AND SEPARATORS
WASH WATER TO SEPARATOR

Figure 7-7. Biazzi continuous-nitration plant.[31]

(Courtesy of John Wiley and Sons, Inc.)

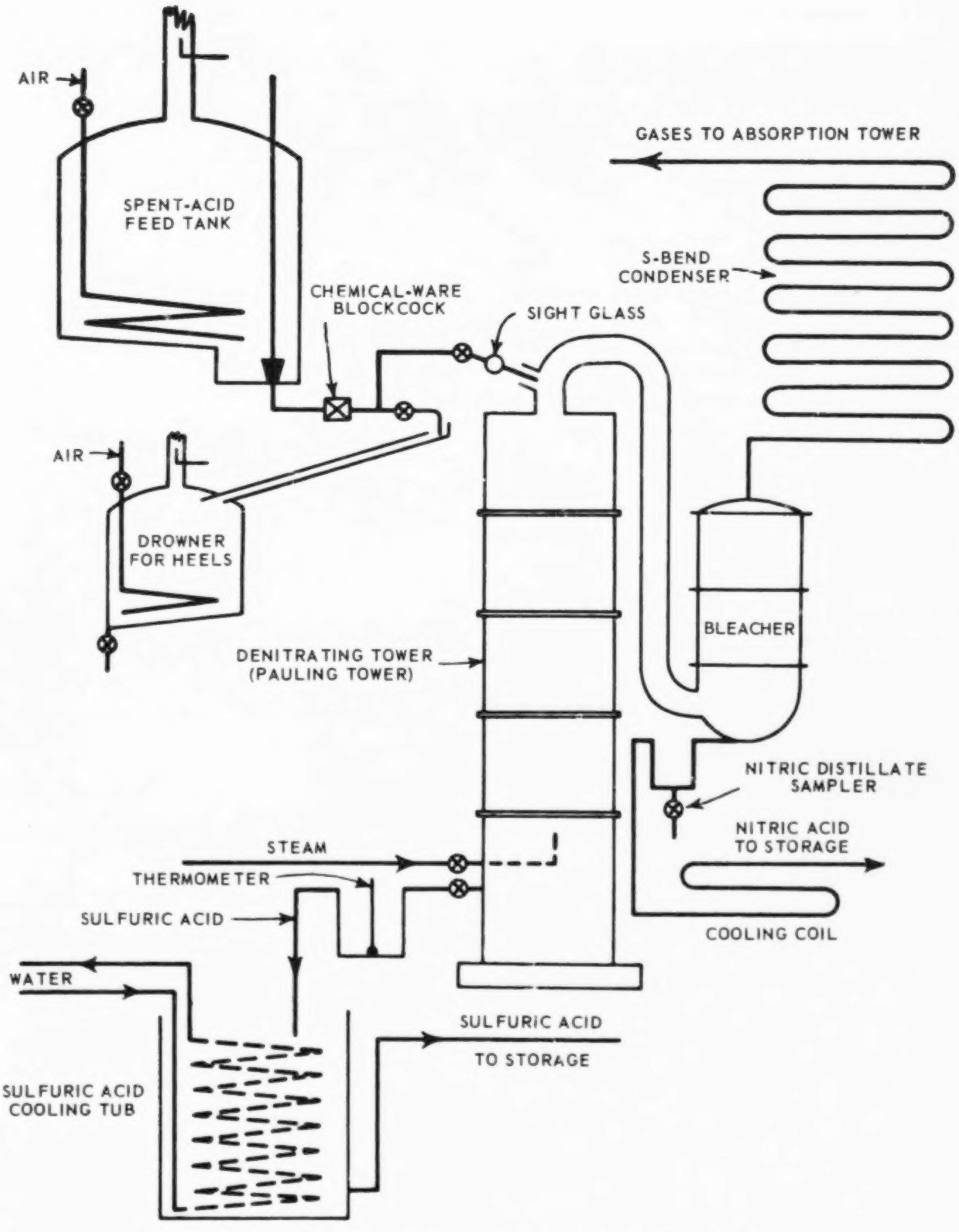

AIR
SPENT-ACID FEED TANK
CHEMICAL-WARE BLOCKCOCK
SIGHT GLASS
GASES TO ABSORPTION TOWER
S-BEND CONDENSER
AIR
DROWNER FOR HEELS
BLEACHER
DENITRATING TOWER (PAULING TOWER)
NITRIC DISTILLATE SAMPLER
NITRIC ACID TO STORAGE
STEAM
THERMOMETER
SULFURIC ACID
COOLING COIL
WATER
SULFURIC ACID TO STORAGE
SULFURIC ACID COOLING TUB

Figure 7-8. Recovery of spent acid.[31]
(Courtesy of John Wiley and Sons, Inc.)

7.2.3.1 *Emissions from Nitration*

Relatively large NO_x emissions may originate in the nitration reactor and in the denitration of the spent acid. NO_x is also released in auxiliary equipment such as nitric acid concentrators, nitric acid plants, and nitric acid storage tanks.

Nitration reactions *per se* do not generate NO_x emissions. NO_x is formed in side reactions involving the oxidation of organic materials. Relatively little oxidation and NO_x formation occur when easily nitratable compounds, such as toluene, are processed. Much more severe conditions are required in processing compounds that are difficult to nitrate, such as dinitrotoluene; more oxidation takes place and, thus, more NO_x is formed.

Very few data are reported in the literature on NO_x emissions from nitrations. For continuous nitrations, one company has reported emissions of 0.12 to 0.24 pound NO_x per ton of nitric acid, with a mean of 0.18 at a single location.[34] At the same location, emissions averaging 14 pounds of NO_x per ton of acid were reported in manufacturing specialty products in small batch-type operations. Further discussion of these small batch nitrations appears in the emission controls section.

Using the factors 0.18 and 14 pounds NO_x per ton HNO_3 as lower and upper limits for nitrations, the NO_x emissions in 1967 would have the range indicated in Table 7-5.

Table 7-5. ESTIMATED NO_x EMISSIONS FROM ORGANIC NITRATIONS IN 1967

Product	Estimated acid consumption, tons/yr	NO_x, tons/yr	
		Lower limit	Upper limit
Nitrobenzene	90,000	8	630
Dinitrotoluene	75,000	7	530

Even using the upper limit, NO_x emissions from nitrobenzene and dinitrotoluene syntheses are relatively small but may present local nuisance problems. Since the upper limit represents specialty batch operations on a small scale, the emissions are probably much higher than would be encountered in large-volume production of these products in either batch or continuous equipment.

7.2.3.2 *Control Techniques*

In large batch or continuous nitrations, operations are carried out in closed reactors. Fumes are conducted from the reactor, air is added, and the mixture enters an absorption tower for recovery of nitric acid. If too much NO_2 remains in the residual gas from the absorber, it may be further reduced by conventional techniques such as caustic scrubbing or fume burning.

NO_x burning is carried out under reducing conditions. An excess of fuel is used, and NO_x acting as an oxidant, is reduced to nitrogen. The system should have at least 10 percent excess fuel. Hardison discusses the fuel/oxidizer ratio limitations in his article.[35] NO_x reductions of 75 percent[36] to 90 percent[35] have been anticipated, but not yet confirmed in plant operation. Burner and flare designs are discussed in references 35 and 37.

Caustic scrubbing of NO_x is discussed in the nitric acid section.

Noncondensable gas from acid denitration is treated in the same manner as reactor gas. A common absorber is sometimes employed.

Small batch nitrators used in manufacturing specialities such as drugs and dyes are small-volume, high-intensity NO_x emitters. In one plant,[34] reaction times ranged from 3 to 12 hours, depending on the product made. From 3 to 850 batches of each product were made each year. Emissions ranged from 1.4 to 260 pounds of NO_x per ton of nitric acid, with a median of 42 pounds per ton of nitric acid. The median emission was 14 pounds per ton when one product was excluded from the calculations. The emissions, which are vented to individual stacks, are brown in color for a few hours per batch

Caustic scrubbing and NO_x incineration were said to be the most plausible controls for specialty batch nitrations. Catalytic reduction is usually ruled out because of organic and other impurities in the gas. Neither control is considered highly efficient in this application.

The intermittent character of emissions makes them difficult to control and contributes to very high pollution abatement costs per ton of nitric acid consumed. Operating costs for such equipment would render approximately half of the small batch nitrations so uneconomical that the manufacture of these products would be terminated.[34] Large batches may be suitable for conversion to continuous operating, but small batches are not.

A potential technique for control of NO_x emissions, which is suitable for some chemical systems, is the addition of urea to the reactants. Urea reacts with N_2O_3 or nitrous acid to form CO_2 and nitrogen. In addition to suppressing NO_x formation, the addition of urea virtually eliminates the oxidation of hydrocarbons.[38]

7.2.3.3 *Costs of Controls*

In large-scale operations, recovery of nitric acid by absorbing concentration NO_x emissions should be economical, as discussed in Section 5 on oxidation. Fume incinerator investments are quoted at $10,000 to $20,000 by one source.[13] Another suggests that investments of $75,000 to $150,000 are necessary for flame abatement facilities for existing small batch nitrators, and $75,000 to $250,000 for existing large nitrators. Annual operating costs were estimated at $25,000 to $85,000 per product for small batch nitrators and $25,000 to $40,000 for continuous nitrators.[34]

7.2.4 Explosives: Manufacture and Use

Industrial explosives in the United States consists of over 80 percent by weight of ammonium nitrate and some 10 percent of nitro organic compounds. The following estimates of ingredients used in commercial explosives (Table 7-6) were derived from statistics of the U.S. Bureau of Mines.[39]

Table 7-6. INGREDIENTS IN U.S. INDUSTRIAL EXPLOSIVES, 1967

Ingredient	Quality, tons
Ammonium nitrate	
Processed and unprocessed	643,000
In permissibles[a]	23,000
In other high-explosives[a]	53,000
In other blasting agents[a]	76,000
Total ammonium nitrate	795,000
Fuel oil, carbonaceous material and other nonexplosive ingredients	120,000[b]
Nitroglycerin	28,000[b]
TNT	10,000[b]
Total	953,000

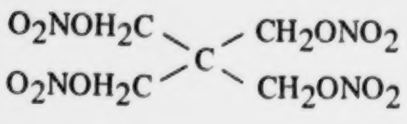
[a] Ammonium nitrate estimated at 65 percent of permissible, 35 percent of other high explosives and 60 percent of water gels and slurries and rigidly cartridged blasting agents.[40,41]

[b] Estimates provided by Du Pont.[18]

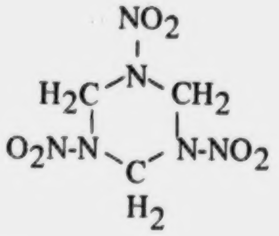
Ammonium nitrate (AN) is widely used because it is the least costly of all explosives, it is very powerful, and it is low in relative hazard. Smaller amounts of other explosives such as nitroglycerin (NG) and trinitrotoluene (TNT) were consumed in commercial explosives in 1967. The manufacture of ammonium nitrate has been discussed above. The manufacture of TNT is included below under military explosives.

Nitroglycerin is manufactured in one stage in both batch and continuous units using mixed acids. Description of specific batch and continuous units are included in the general description of nitration above. Anhydrous mixed acid containing 45 to 50 percent HNO_3 and 50 to 55 percent H_2SO_4 is the most common nitrating agent. Nitric acid consumption is about 1 pound of nitroglycerin.[42] TNT also requires about 1 pound of nitric acid per pound of product.[33] The estimated consumption of nitric acid in 1967 in commercial explosives, other than ammonium nitrate, was 38,000 tons, based on 10,000 tons of TNT and 28,000 tons of nitroglycerin, as shown in Table 7-6.

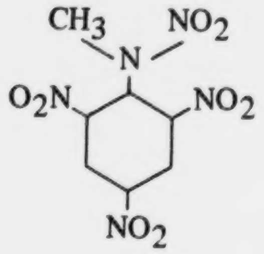
Production and consumption data for military explosives are classified. Some of the more important ingredients in military explosives are known however: TNT, penterythritol tetranitrate (PETN), cyclotrimethylene-trinitramine (RDX), and trinitrophenylmethylnitramine (Tetryl). Nitration is an essential step in the manufacture of each of these. The structures of PETN, RDX, and Tetryl are shown above.



PETN



RDX



Tetryl

PETN is most commonly used in conjunction with TNT in the form of pentolites, made by incorporating PETN into molten TNT. RDX is used in admixture with TNT, or compounded with mineral jelly to form a useful plastic explosive. Tetryl is most often used as a primer for other less sensitive explosives. Methods of preparation of these explosives are discussed in detail by Urbanski.[33]

TNT (symmetrical trinitrotoluene) is produced in batch and continuous processes. The addition of each successive nitro group to the toluene molecule becomes more difficult, so that more servere conditions are required. Therefore, it is normal practice to introduce strong mixed acids at one end and toluene at the other in a multistage-operation as illustrated in Figure 7-9.

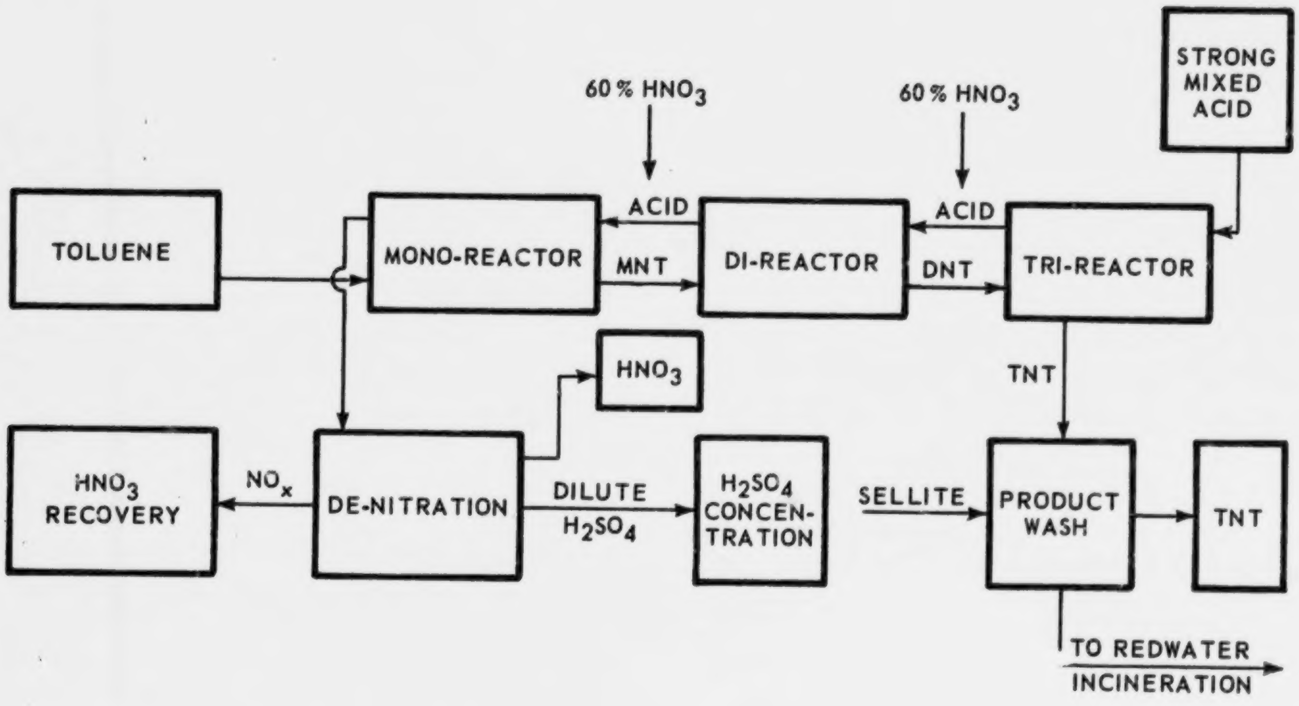

60 % HNO3
60 % HNO3
STRONG MIXED ACID
TOLUENE
MONO-REACTOR
ACID
MNT
DI-REACTOR
ACID
DNT
TRI-REACTOR
HNO3
TNT
HNO3 RECOVERY
NOx
DE-NITRATION
DILUTE H2SO4
H2SO4 CONCEN-TRATION
SELLITE
PRODUCT WASH
TNT
TO REDWATER INCINERATION

Figure 7-9. Trinitrotoluene (TNT) manufacturing diagram.

The spent acid leaving one stage is fortified with fresh nitric acid before entering the next stage. The spent acid from the final stage is denitrated in equipment illustrated in Figure 7-5. Nitric acid is recovered from the denitrator overhead, for recycling to the process, and the uncondensable gas is sent to an absorption tower to recover NO_x as nitric acid.

TNT is purified by washing with sodium sulfite (Sellite). The principal impurities are asymmetrical trinitrotoluenes, which react rapidly with sodium sulfite to form dinitrotoluene sulfonates, which are soluble in the wash water. The waste wash water is disposed of by evaporation, the residue being incinerated.[33] The waste water has a deep red color from the nitro compounds and is generally referred to as "redwater."

Operating conditions for nitrating dinitrotoluene to trinitrotoluene are severe—anhydrous mixed acid, and temperatures of 100° C and higher. Yields of 82 to 90 percent of theoretical are typical, because of oxidation reactions that generate carbon oxides and NO_x.[33] It is, therefore, essential to process the reactor fumes as well as the denitrator uncondensibles in an absorption tower to minimize net acid consumption.

For discussion of the various processes used in manufacturing TNT, the reader is referred to Urbanski's book.[33]

7.2.4.1 Emissions

NO_x emissions from TNT nitration reactors at the new Ordnance Works at Newport, Indiana, have been estimated at approximately 2.5 pounds per ton of TNT. The NO_x concentration, diluted with 14 volumes of air, was estimated at 400 ppm.[36]

Much higher NO_x emissions were reported at another ammunition plant where the equipment was old and overloaded. This plant has been an intense source of NO_x, generating about 130,000 pounds of NO_x per day.[43,44] A program is planned to reduce emissions.

Assuming that the average TNT plant would emit twice as much NO_x as the new plant mentioned above, and that no NO_x is emitted in nitroglycerin manufacture,[18] NO_x emisisons from commercial explosives (Table 7-6) are roughly estimated in Table 7-7.

Redwater destruction is not employed in manufacturing TNT for commercial use[18] because redwater is not made. In contrast, redwater production accompanies manufacture of military TNT because of the necessity for washing out isomers and other impurities that make TNT sensitive to shock. Military ammunition must be capable of long storage and must be insensitive to handling.

Other sources of NO_x related to explosives manufacturing are denitration of spent mixed acid, nitric acid concentration, and nitric acid production.

At the Newport plant, emission from denitration and nitric acid concentration were estimated at about 12 pounds per ton of nitric acid after 75 percent reduction in a fume burner. The NO_x concentration was estimated at 1.7 percent, probably all NO.

Oxygen balance is the most important factor affecting the NO_x content of the products of explosions. An oxygen-balanced explosive contains just enough oxygen to

Table 7-7. TOTAL UNITED STATES NITRIC ACID REQUIREMENTS AND NO_x EMISSIONS FROM MANUFACTURE OF INDUSTRIAL EXPLOSIVES, 1967

	Product, tons	HNO_3, tons	NO_x, lb/ton HNO_3	NO_x, tons/yr	No_x, ton/ton of product
TNT (industrial use)	10,000	10,000			
Reactor			5.0	25	0.003

oxidize all carbon in the explosives to carbon dioxide and all hydrogen to water. A deficiency of oxygen produces toxic carbon monoxide whereas an excess of oxygen tends to produce NO_x.[40,41] Ammonium nitrate itself contains an excess of one atom of oxygen per molecule. Combustible materials, e.g., 5 percent fuel oil, are usually added to ammonium nitrate to provide oxygen balance and increase power. Nitroglycerin has a slight oxygen surplus, while TNT is short of oxygen.

Compositions of the products of explosions are difficult to determine. For this reason, most of the information on these products is obtained by detailed computer calculations. The reader is referred to Cook's book for information on methods of calculations.[40] NO_x is found in explosion products when the explosive contains more oxygen than required for oxygen balance. Calculated NO_x in products from various explosives are listed in Table 7-8.

The volume of NO_x generated in commercial explosions in 1967 was probably less than 100 tons since most of the 28,000 tons of nitroglycerin was used in oxygen-balanced explosives.[18]

Although a very small source of NO_x emission, explosions could be an intense source in confined spaces underground, and precautions should be taken to avoid exposure in such places.

7.2.5 Other Uses of Nitric Acid

Other uses of nitric acid include acidulation of phosphate rock and limestone for use in fertilizers, the treating of metals, and rocket fuel oxidation.

7.2.5.1 Fertilizers

In the United States, sulfuric and phosphoric acids are the principal acids used in acidulating phosphate rock. A few manufacturers produce "nitric phosphate" fertilizers by acidulating phosphate rock with nitric acid to form phosphoric acid and calcium nitrate. In subsequent steps, ammonia is added with either carbon dioxide, or sulfuric or phosphoric acid, and "nitric phosphates" are formed. Dibasic calcium phosphate and ammonium nitrate are the useful compounds produced.[45]

U.S. Department of Agriculture statistics[46] do not segregate nitric phosphate fertilizers made by acidulation of phosphoric rock; but private sources indicate that nitric phosphate fertilizer made in this manner was estimated at 500,000 tons in 1967, and nitric acid consumption at 150,000 tons.

NO_x emissions are dependent on the quantity of carbonaceous material in the rock, since NO_x is formed as nitric acid oxidizes the carbonaceous matter. The use of calcined rock avoids the production of NO_x.

Air pollution abatement by fertilizer manufacturers' efforts has centered on reducing

Table 7-8. NO_x IN PRODUCTS OF EXPLOSIONS

Explosive	NO_x, %	NO_x, lb/ton explosives
TNT, 50/50 Amatol, RDX, tetryl, straight dynamites, AN=fuel oil	0	0
AN/DNT	0	0
PETN	0.3-0.6	10-18
Nitroglycerin	1.5	46
Straight gelatins, 40%	0.1	3
Straight gelatins, 75%	0.1	3

particulates and fluorides emissions, which are severe problems. The water scrubbing used to reduce these pollutants would be expected to reduce NO_X emissions to only a minor degree. Although no measurements of NO_X emissions are available, brown plumes are said to occur.

One company[47] has found that the addition of urea to the acidulation mixture reduces NO_X emissions and eliminates the brown plume.[47] Urea, as mentioned in the discussion on nitration controls, reacts with NO and NO_2 to form N_2.

7.2.5.2 Metals Pickling

The principal use of nitric acid in metals pickling is in treating stainless steel. Mill scales on stainless steels are hard and are difficult to remove. Pickling procedures vary; sometimes a 10 percent sulfuric acid bath at 140° to 160° F is followed by a bath at 130° to 150° F with 10 percent nitric acid and 4 percent hydrofluoric acid. The first bath loosens the scale, and the second removes it. A continuous system for stainless steel strip consists of two tanks containing 15 percent hydrochloric acid, followed by a tank containing 4 percent hydrofluoric and 10 percent nitric acid at 150° to 170° F. One effective method is the use of molten salts of sodium hydroxide to which is added some agent such as sodium hydride. This may be followed by a dilute nitric acid wash.[48]

Nitric acid is preferred to other acids for treating stainless steel because it does not attack the steel itself. Sulfuric and hydrochloric acids, which are less costly, are usually preferred for other metals.

No measurements were found of emission rates from nitric acid pickling of stainless steel. Treating equipment should be properly hooded and ventilated and the fumes scrubbed to protect workers. Urea would probably control the NO_X emissions.

Nitric acid is also used in the chemical milling of copper or iron from metals that are not chemically attacked by nitric acid, and for bright-dipping copper. In the latter operation, a cold solution of nitric and sulfuric acid has been customarily used. It has been reported that copper can be bright-dipped in cold nitric acid alone when urea is added. A highly acceptable finish is obtained, and NO_X fumes are eliminated.

Sulfuric acid should not be used with the nitric acid-urea mixture since nitrourea, an explosive, can form. Not more than 8 ounces of urea per gallon should be added, and satisfactory operation can be obtained with only 2 ounces per gallon.

In chemical milling, the addition of 6 to 8 ounces of urea per gallon of 40 percent nitric acid will reduce NO_2 emissions from 8,000 ppm to levels below 10 ppm, providing a bubble disperser is used.[49]

A small, but intense, source of NO_X occurs in the manufacture of tungsten filaments for lightbulbs. Tungsten filaments are wound on molybdenum cores, and after heat-treating, the cores are dissolved in nitric acid. Decker[13] describes air pollution equipment for reducing the dense NO_2 fumes given off periodically when trays of the filaments are dissolved. The fumes pass over a charcoal adsorber bed, which adsorbs NO_X as fumes are generated and desorbs when no fumes are being generated. This smooths out peaks and valleys in NO_X content in offgases, which are then heated and combined with carbon monoxide and hydrogen from a rich combustion flame. The mixture is then passed through a bed of noble metal catalyst. A colorless gas is released from the equipment.

7.3 PETROLEUM AND NATURAL GAS INDUSTRIES

Oil and gas production, pipeline transportation, gas plant operation, and petroleum refining as stationary sources of NO_X are discussed in this section. Tanker, barge, truck, and rail transportation, since they are mobile sources of NO_X, are not covered.

Major power consumers in oil and gas production operations include drilling, oil well pumping, gathering, gas and water injection to the producing formation, and oil dehydration. Gas plant operations include removal of impurities, such as water and surface compounds, and recovery of valuable natural gas liquids, such as ethane, propane, butane, and natural gasoline.

In petroleum refining, crude oil is converted into salable products in the required volumes. A simplified flow sheet for a refinery appears in Figure 7-10. Crude oil is charged to an atmospheric pipestill where light products are separated and taken overhead and light catalytic reforming feed, raw gasoline, kerosene, middle distillate, and heavy gas oil are taken as sidestream products. The reduced crude is charged to a vacuum pipestill where heavy gas oil, lube stocks, and residuum are cut.

Atmospheric and vacuum gas oils are charged to catalytic cracking units, which produce light ends, cracked gasoline, and fractions for blending distillate and residual fuels. Reduced crude is used in making asphalt or residual fuels, and is often fed to coking to increase the yield of distillate products.

Catalytic cracking and coking produce propylene and butylene, which are often alkylated with isobutane to make alkylate. Sometimes the olefins are polymerized for gasoline or chemical production. Catalytic reforming increases the octane number of naphtha by converting naphthenes (saturated cyclic hydrocarbons) and paraffins to aromatics. Hydrogen treating is used to reduce sulfur content, increase stability, and improve burning characteristics of kerosenes and middle distillates.

The relative volumes of gasoline, kerosene, middle distillate, heavy fuel oil, etc., can be adjusted by diverting heavy gasoline fractions from gasoline to middle distillate and cat-cracking feed, by diverting coker feed to heavy fuel, etc.

A fluid-bed catalytic-cracking unit is often the heart of a modern refinery. Such a unit is illustrated in Figure 7-11. Preheated gas oil is charged to a moving stream of hot regenerated catalyst while it is being transferred from the regenerator to the reactor. The gas oil is cracked in the reactor; the products then pass through cyclone separators for removal of entrained catalyst and are cut into products in a fractionator. Coke forms on the catalyst during the reaction.

Spent catalyst is withdrawn from the bottom of the reactor and transferred to the regenerator where coke is burned off. The regenerator flue gas passes through cyclone separators for catalyst removal and is discharged through the stack. The hot, regenerated catalyst flows back to the reactor, supplying heat and catalyzing the cracking reaction.

The regenerator flue gas contains about 10 percent carbon monoxide. This gas is sometimes fed to a CO boiler where it is burned in the preheated air to generate steam. Auxiliary fuel is required to maintain satisfactory combustion conditions.

Typical refinery process heaters are the cabin-type furnace, used for heat releases above 150 million Btu per hour, and the vertical cylindrical furnace, used for heat duties below 80 million Btu per hour. Either type may be used in the 80- to 150-million-Btu-per-hour range. Combustion boxes are lined with refractory. Fuels may be liquid, gas, or a combination of both. Gas burners operate with 10 to 40 percent excess air, liquid burners with 20 to 80 percent. Stack temperatures are 400° to 900° F.

7.3.1 Emissions

NO_X emissions in the petroleum and natural gas industries result from the combustion of fuel in process heaters and boilers, and from internal combustion engines used to drive compressors and electric generators. NO_X is also released from the catalytic-cracking regenerator and from CO boilers.

Oil and gas production, gas plants, and pipeline stations are usually located in remote areas far from population centers. Emissions do not, therefore, contribute substantially to NO_X levels in populous areas. Petroleum refineries, however, are often located in or near densely populated areas.

Estimates of the amounts of NO_X emitted from petroleum and natural gas operations in the year 1967 are shown in Table 7-9.

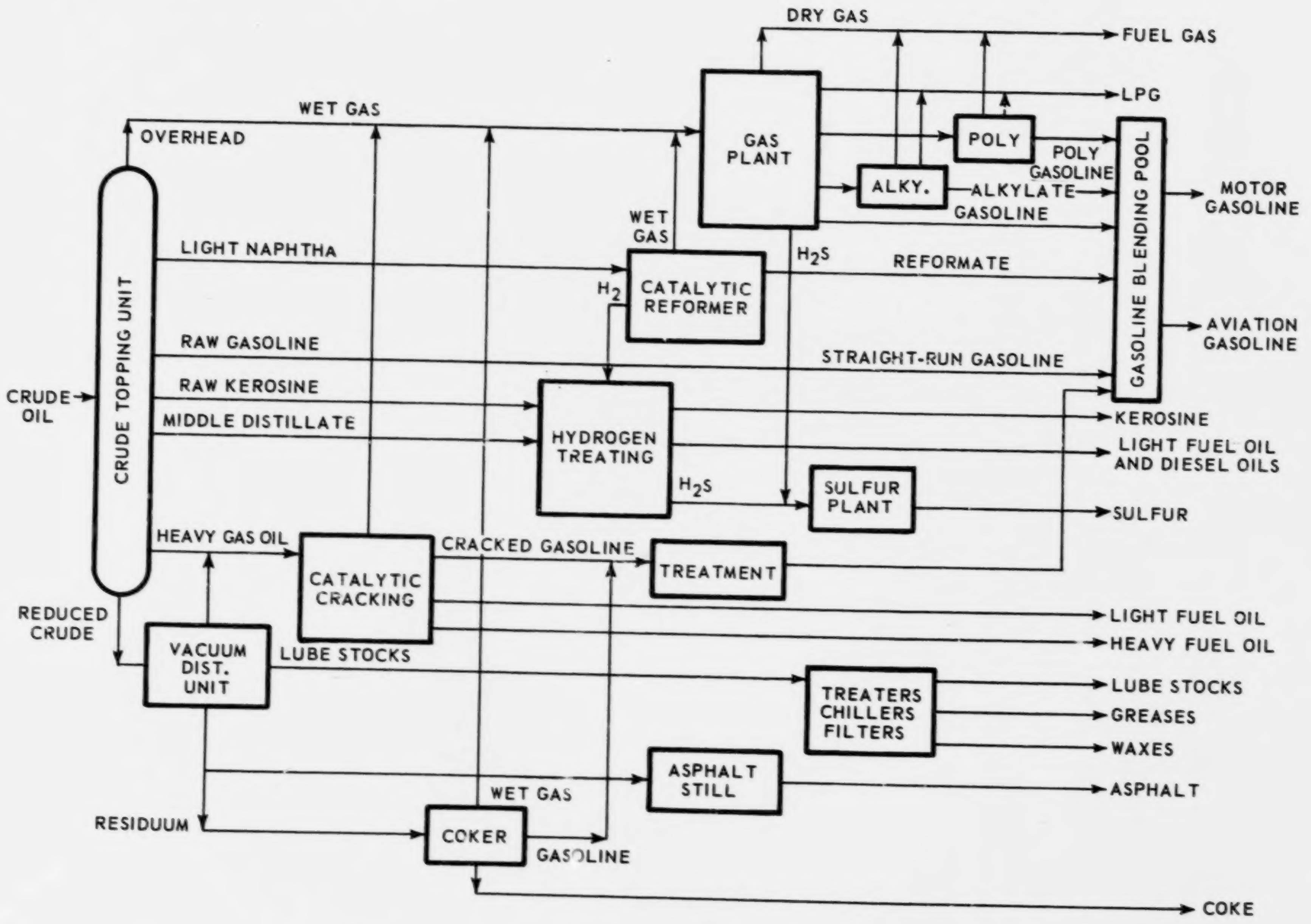

DRY GAS
FUEL GAS
LPG
WET GAS
OVERHEAD
GAS PLANT
POLY
POLY GASOLINE
ALKY.
ALKYLATE
GASOLINE
GASOLINE BLENDING POOL
MOTOR GASOLINE
WET GAS
LIGHT NAPHTHA
H_2
CATALYTIC REFORMER
H_2S
REFORMATE
CRUDE TOPPING UNIT
AVIATION GASOLINE
RAW GASOLINE
STRAIGHT-RUN GASOLINE
CRUDE OIL
RAW KEROSINE
MIDDLE DISTILLATE
HYDROGEN TREATING
KEROSINE
LIGHT FUEL OIL AND DIESEL OILS
H_2S
SULFUR PLANT
SULFUR
HEAVY GAS OIL
CATALYTIC CRACKING
CRACKED GASOLINE
TREATMENT
REDUCED CRUDE
LIGHT FUEL OIL
HEAVY FUEL OIL
VACUUM DIST. UNIT
LUBE STOCKS
TREATERS CHILLERS FILTERS
LUBE STOCKS
GREASES
WAXES
ASPHALT STILL
ASPHALT
WET GAS
RESIDUUM
COKER
GASOLINE
COKE

Figure 7-10. Composite processing plan for a modern refinery.

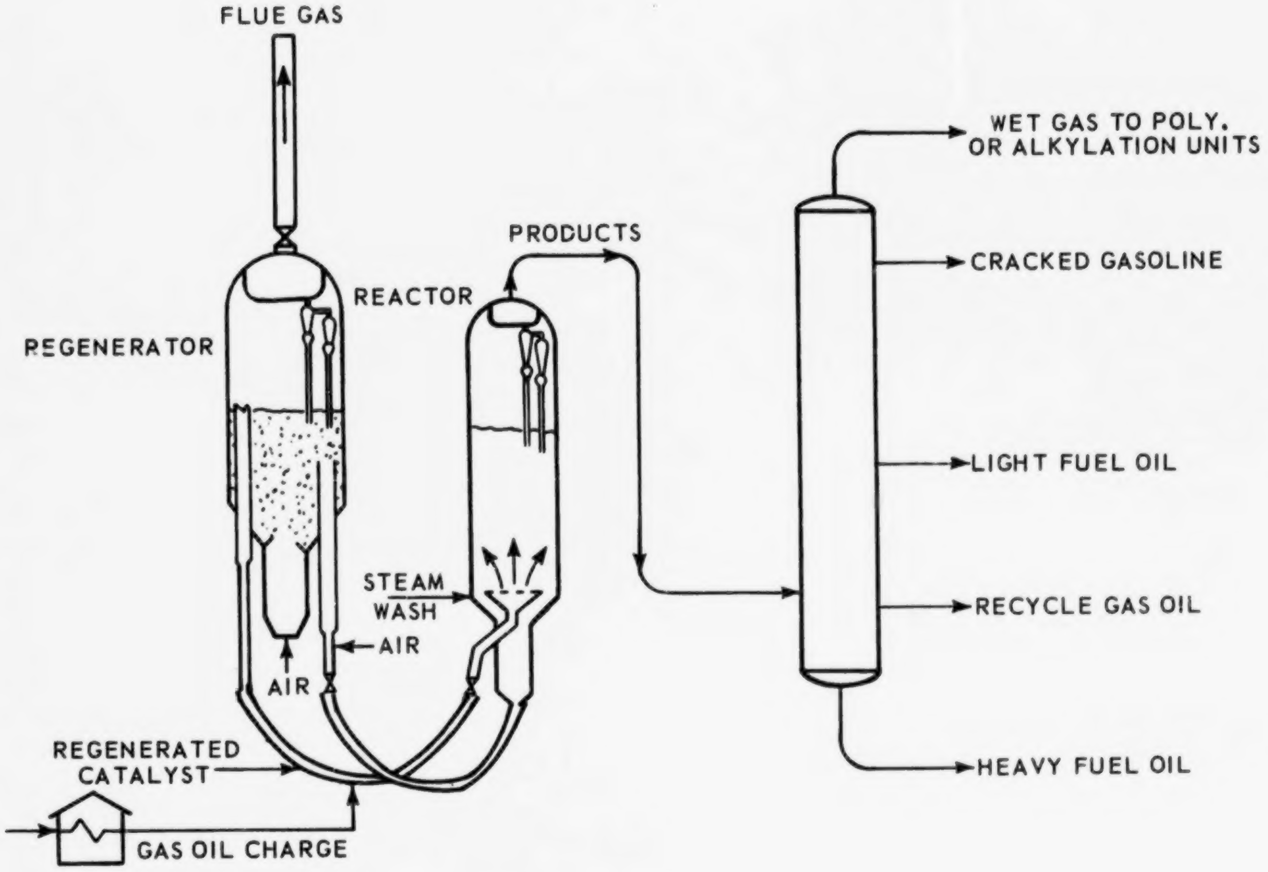

FLUE GAS
WET GAS TO POLY. OR ALKYLATION UNITS
PRODUCTS
CRACKED GASOLINE
REACTOR
REGENERATOR
LIGHT FUEL OIL
STEAM WASH
AIR
RECYCLE GAS OIL
AIR
REGENERATED CATALYST
HEAVY FUEL OIL
GAS OIL CHARGE

Figure 7-11. Fluidized bed catalytic cracking unit (FCC).

Diesel oil consumption given in Table 7-9 was taken as residual plus diesel fuel oil consumed in "oil-company use,"[54] minus fuel oil "consumed at refineries."[53] All diesel oil consumed in oil and gas production was assumed to have been used in diesel engine prime movers, the use with the highest emission factor. Gas consumed in oil and gas production was estimated by subtracting gas used in gas plants and estimated losses, from the gas field use.[50]

Under "refining" in Table 7-9, the numbers shown for gas include natural gas, LPG, and refinery gas, calculated as natural gas on the basis of heat of combustion.[53] Oil consumption includes acid sludge.[53]

Allocation of gas plant fuel among "heaters and boilers," "gas engines," and "gas turbines" is based on a survey of sources of NO_X emissions in the oil and gas industries conducted by Esso Research and Engineering Company and funded by the National Air Pollution Control Administration under Contract No. PH 22-68-55.[51,56] Allocation of pipeline fuel between "gas engines" and "gas turbines" is based on capacities indicated by *Pipe line Industry.*[57] Allocation of gaseous fuels to the various users in refineries is based on the industry survey conducted by Esso.[51,56]

Emission factors for gas-fired heaters are derived from Figure 7-12. This relationship between NO_X production rate and fuel-firing rate is based on emission data obtained in the petroleum and natural gas survey.[51,56] Emission factors for diesel engines and oil-fired furnaces are taken from Duprey[55] Emission factors for gas engines are based on Figure 7-13, which is reproduced from the studies of Mills[14] et al. Emission factors for gas-turbine

Table 7–9. NO_x EMISSIONS FROM PETROLEUM AND NATURAL GAS OPERATIONS, 1967

Operations	Fuel consumption[a]	Emission factor[b]	NO_x emissions	
			Range, ppm	Quantity, 10^3 ton/yr
Oil and gas production				
Gas				
Heaters and boilers	495[c]	200[d]	25-200	50
Engines	124[c]	770[e]	250-2,500	48
Oil				
Diesel engines	7.3[f, g]	220[h]		34
Production subtotal				132
Gas plants				
Heaters and boilers	247[c]	190[d]	25-200	24
Engines	260[c]	4,300[e]	1,000-3,500	561
Turbines	15[c]	200[i]	50-200	2
Gas plant subtotal				587
Gas pipelines				
Engines	436[c]	7,300[e]	1,500-3,500	1,596
Turbines	140[c]	200[i]	50-200	14
Gas pipeline subtotal				1,610
Refining				
Gas				
Heaters and boilers	1,656[f]	210[d]	25-200	173
Engines	40[f]	4,350[e]	1,000-3,500	87
Turbines	54[f]	200[i]	50-200	5
Oil				
Heaters and boilers	39.7[f]	67[h]	50-400	56
Other				9
Refining subtotal				330
Total NO_x emissions				2,659

[a] Oil consumption as million bbl/yr.
Gas consumption as billion scf/yr.
[b] Oil emission factors - lb NO_x/1,000 gal.
Gas emission factors - lb/million scf.
[c] Reference 50.
[d] Reference 51.
[e] Reference 52.
[f] Reference 53.
[g] Reference 54.
[h] Reference 55.
[i] See Table 5-3.

engines were from Table 7-9. Furnace and engine sizes in the various applications are also based on the survey of the petroleum and natural gas industry.[51,56]

Other emissions in refining include NO_x produced in catalytic-cracking regenerators (3,000 tons per year), and NO_x from carbon monoxide burned in CO boilers (6,000 tons per year). The emissions from catalytic-cracking regenerators result from cracking 4,190 thousand barrels of fresh feed per day[58] at an emission rate of 4.2 pounds NO_x per thousand barrels.[59] There are 75 CO boilers in the United States,[8] each emitting an estimated 21 pounds per hour of NO_x.

Catalytic-plant regenerator gas emission factors were derived from the data reported

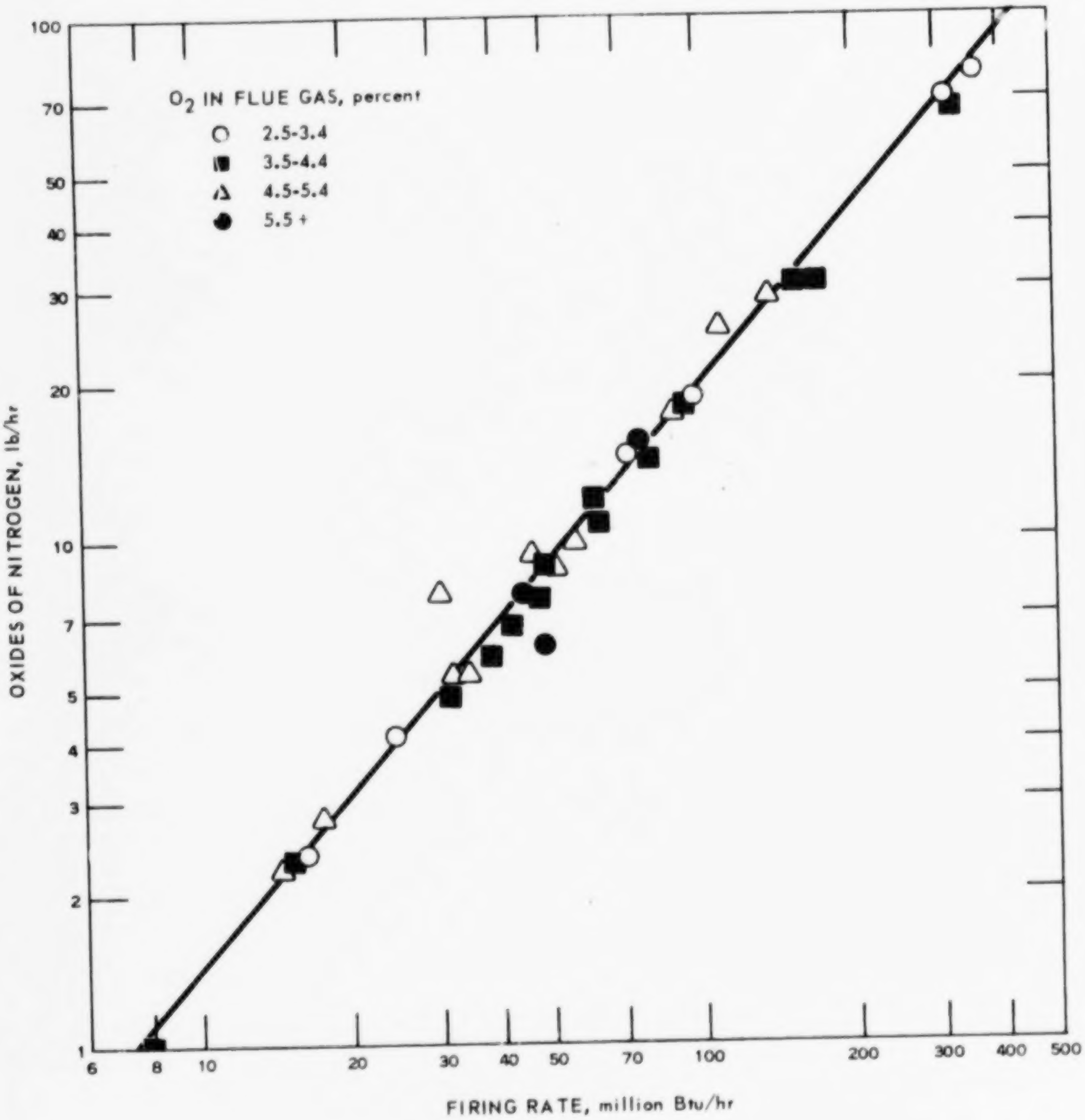


Figure 7-12. Oxides of nitrogen emissions from refinery furnace.[51]

by Mills[59] et al., since the factors reported by Duprey[55] were based on data which have been superseded.[59] The 4.2 pounds per thousand barrels of fresh feed is a weight average emission factor for fluid and moving-bed catalytic-cracking units. NO$_X$ in catalytic-cracker flue gas would be about 10 times as high, based on Duprey's factors,[55] which are not consistent with other data now available.

CO boiler factors were based on recent tests by an oil company.[6] The data reported by Mills[59] et al. would give 45 x 10^3 tons per year of NO$_X$. This is greater than the amount generated in a conventional furnace with

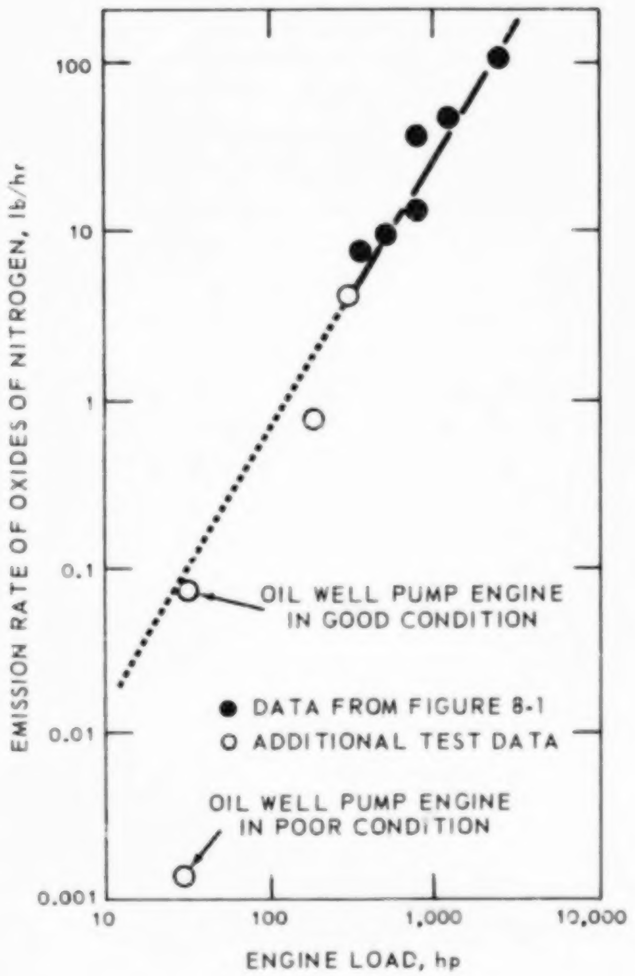


Figure 7-13. Variation in oxides of nitrogen emission rates from stationary internal combustion engines.[52]

much higher flame temperatures; the emission factor is therefore thought to be too high.

Emission factors for gas engines are not firmly established. In Figure 7-13, the high values for large engines reported by Mills et al. are believed to reflect lean combustion mixtures, supercharging, low speed, and other factors that favor high NO_x emissions. (See Section 5.3.) The values for smaller engines reported by Mills[60] et al. are probably for naturally aspirated engines, operated at higher speed with rich combustion mixtures–factors that favor low NO_x The position of the points on the plot probably reflect these factors, not size *per se*. Thus, the correlation shown in Figure 7-13 is used as a means of interpolation in estimating emissions. Extrapolation of the correlation for engines larger than 2,000 horsepower (hp), the largest size tested, was avoided and emission factors derived for the 2,000-hp engine were applied to larger engines.

It should be emphasized that only meager data are available for gas engines, and the emission factors may not be truly representative. The use of Duprey's gas engine emission factor, based on tests of engines averaging about 350 hp[52] would result in estimated pipeline and gas plant emissions of only 200,000 and 140,000 tons per year of NO_x.

NO_x emissions from the petroleum and natural gas industries as a percentage of total NO_x from all sources in the United States are given in Table 7-10.

Table 7–10. NITROGEN OXIDE EMISSIONS FROM PETROLEUM AND NATURAL GAS OPERATIONS IN UNITED STATES, 1967

Petroleum and natural gas operations	Percent of total 1967 emissions
Oil and gas production	0.8
Gas plant	3.7
Pipeline	10.3
Refining	2.1
Total	16.9

7.3.2 Control Techniques

Control of emissions from steam boiler operations has been covered in Section 5.1. Combustion modifications such as low excess air, flue gas recycle, two-stage combustion, and steam or water injection may be applicable to both boilers and refinery heaters.

Flue gas recirculation has potential as an NO_x control method for process furnaces. It could be incorporated into new furnaces and installed in existing furnaces. Several factors mitigate against two-stage combustion and very low excess air rates in process furnaces. Excellent combustion conditions are required to prevent hot spots and coking inside furnace tubes as well as corrosion of tube hangers. Two-stage combustion produces long smoky flames which impinge on furnace tubes. Most furnaces are of natural draft design, and the air rate is controlled by damper setting. Furthermore, many furnaces burn by-product gas or liquid fuels of fluctuating composition and heat content. Thus, inadequate control of air rate and fluctuating fuel quality limit the reduction in excess air.

Potential methods of controlling emissions from spark-fired gas engines include adjusting fuel/air ratio, reducing intake manifold pressure, water injection, and exhaust gas recirculation. Tests on laboratory engines indicate that water injection into the intake manifold reduces NO_x with no decrease in maximum power or fuel economy.[61] At 93 percent of theoretical fuel, NO_x was reduced from 3,000 ppm with no water injection to about 700 ppm at a water injection rate of 1.25 pounds per pound of fuel. Water injection was even more effective for rich mixtures.

Operation with rich rather than lean mixtures reduces NO_x, but increases fuel consumption and CO and hydrocarbon emissions. The NO_x can potentially be reduced to N_2 in a catalytic reactor making use of the unburned hydrocarbons and carbon monoxide in the exhaust gas from fuel rich combustion. A second reactor may be needed to oxidize the CO and hydrocarbons.

In engines burning natural gas, fuel/air ratios as low as 70 percent of stoichiometric may be employed without misfiring. The narrower flammability limits for gasoline cause misfiring at such lean conditions. A laboratory engine burning methane at 70 percent of stoichiometric fuel produced only about 30 percent of the NO_x produced at 92 percent of stoichiometric methane.[62] The latter operation is typical of many engines and produces maximum NO_x. Operation with very lean mixtures results in a loss of maximum power, but fuel economy apparently was not reduced in a laboratory engine.[62]

Reduction of manifold pressure as limited by maximum speed tends to reduce NO_x at the expense of fuel economy.

NO_x emissions can be cut, over a long period, by using gas turbine drivers in new installations and replacing wornout units with gas turbines. Gas turbines consume about 11,000 Btu per horsepower-hour compared to about 6,600 for piston engines.[57] The cost of modified aircraft turbines, however, are about $110 per horsepower compared with about $300 for reciprocating engines.[57] The current trend is toward turbines that are better adapted to automation.

NO_x from diesel engines may be reduced by the use of precombustion instead of direct injection. Variable compression ratio, two-stage fuel injection, and exhaust gas recycle may be helpful. (See Section 5.2.)

7.3.3 Costs of Control

Cost estimates were made for two recent refinery furnace designs and are tabulated in Table 7-11. Input rates of 50 million and 300 million Btu per hour, respectively, were selected as being representative of the sizes presently found in refineries. Estimates for other sizes may be extrapolated from these data. Cost estimates were made only for flue gas recirculation control, other control techniques not being suitable to this equipment, as discussed in Section 7.3.2.

7.4 METALLURGICAL PROCESSES

7.4.1 Furnaces Related To Hot Metal Or Pig Iron Production

7.4.1.1 Blast Furnace

The blast furnace is the central unit in which iron ore is reduced, in the presence of coke and limestone, for the production of pig iron. The blast furnace itself is normally a closed unit and therefore has no atmospheric emission. A preheated air blast is supplied to the furnace from the blast furnace stove, through nozzle-like openings called tuyeres. The subsequent reactions in the blast furnace are not pertinent to this discussion. Excellent descriptions are available, however, such as the complete discussion of the process of changing raw ore to finished steel published by United States Steel Corporation.[63]

The hot blast reacts with the coke to produce heat and carbon monoxide. The excess carbon monoxide, beyond that needed

Table 7–11. INVESTMENT COST ESTIMATES FOR REFINERY FURNACES IN TWO SIZES, AT A STANDARD LOCATION, WITH NITROGEN OXIDES CONTROL BY FLUE GAS RECIRCULATION, APRIL THROUGH JUNE 1969[a], [51]

Investment	Furnace No. 1[b]	Furnace No. 2[c]
No recirculation		
Material	$133,900	$ 712,500
Labor	27,000	152,700
Total	$160,900	$ 865,200
30 percent recirculation		
Material	$151,100	$ 867,000
Labor	29,900	$ 180,000
Total	$181,000	$1,047,000
Increased horsepower required by 30 percent recirculation		
Installed	89 hp	530 hp
Operating	63 hp	386 hp

[a] Basis of estimates: only furnace equipment costs, including blowers, are reflected in costs. Nonequipment costs (i.e., foundations, site preparation, instrumentation, feed piping) and contractor's field labor overhead and fees, are not included.

[b] 50 million Btu/hr, vertical cylindrical, heat absorbed.

[c] 300 million Btu/hr, vertical tube cabin, heat absorbed.

in reducing the ore, leaves the top of the blast furnace with other gaseous products and particulates and is known as blast furnace gas. This gas is cleaned to remove the particulates, which could later cause plugging. It is then available for heating purposes. Blast furnace gas contains about 1 percent hydrogen and 27 percent carbon monoxide; it has a heating value of approximately 92 Btu/ft^3.[64]

7.4.1.2 Blast Furnace Stove

Between 4 and 5 tons of blast furnace gas is generated for each ton of pig iron produced. Some 18 to 24 percent of this gas is used as fuel to heat the three stoves which are usually associated with each blast furnace. Two are generally on heat while the third is on blast.

The blast furnace stove is a structure some 26 to 28 feet in diameter and about 120 feet high. A roughly cylindrical combustion chamber extends to the top of structure and the hot combustion gases pass through a brick checkerwork to the bottom by reverse flow and thence to the stack. The checkerwork usually contains 275,000 square feet of heating surface and has about 85 percent thermal efficiency. Unlike the conventional regenerators, which extract heat from the waste combustion gases, the blast furnace stove is heated by burning fuel. The stored heat is then used to preheat air for the combustion of fuel in the furnace to be served.

The low calorific value of blast furnace gas would indicate that due to dilution and low flame temperature the NO_x content of the combustion gas from blast furnace stoves should be low. A steel manufacturer who requests annonymity gives data on stack gas samples ranging from 1.7 to 6.6 ppm NO_x, or an average of 3.6 ppm. However, the NO_x emission based on the Btu output is estimated at 26 pounds NO_x per hour or 114 tons per year for a typical blast furnace.* On June 1, 1968, there were 173 furnaces on blast in the United States,[66] which indicates an annual atmospheric burden of 20,000 tons of NO_x from blast furnace operations. This is 0.7 percent of the estimated 1965 total industrial NO_x emissions[67] in the United States.

7.4.2 Furnaces Related to Steel Production

7.4.2.1 Open Hearth Furnace

Steel making by the open hearth process has been decreasing since it reached a peak in 1956, when it represented 90 percent, or 103 million tons, of the total production. In 1967, production had declined to 55 percent and by 1972, only 25 million tons may be so-produced. Phase-out is expected between 1980 and 1990.[68] Regardless of this dramatic decline in the use of the open hearth process, due to the inroads of basic oxygen furnace steelmaking processes, its NO_x emission potential deserves consideration.

The open hearth furnace is both reverberatory and regenerative, like the glass melting furnaces (see Section 7.6). It is reverberatory in that the charge is melted in a shallow hearth by heat from a flame passing over the charge and by radiation from the heated dome. It is regenerative in that the remaining heat in the partially spent combustion gases from the reverberatory chamber is accumulated in a brick-filled chamber, or "checker", and released to preheat the incoming combustion air when the cycle is reversed. Fuel of low calorific value such as blast furnace gas as well as the combustion air may be preheated by the checkers in order to obtain the high temperatures required.

Hot metal from the blast furnace, pig iron, scrap iron, and lime are the usual materials charged to an open hearth furnace. These are heated over a period averaging 10 hours, at a temperature as high as the refractories will permit. Fuel oil is the preferred fuel and is burned with excess air to provide an oxidizing influence on the charge. These conditions favor NO_x formation, and an analysis of 10 open hearth stack samples shows an emission range of 22.9 to 671 ppm, or an average of 243 ppm. In another series of tests, an average of 320 ppm was obtained. These analyses were taken while an oxygen lance was being used to enhance the steel producing reactions.[69]

It is estimated that 490 pounds of NO_x is emitted in the production of a 200-ton batch of steel. These calculations are based on 3.2 million Btu of fuel per ton of steel[70] and 0.76 pound of NO_x per million Btu. If the United States production of steel in 1967 was 127,213,000 tons[70] and 55 percent was produced in open hearth furnaces, then roughly 85,000 tons of NO_x was emitted to the atmosphere from these sources. This represents 3.1 percent of the estimated 1965 industrial NO_x emissions in the United States.[68]

7.4.2.2 Coking Ovens

Coke is an essential component in making pig iron and steel; coke ovens are generally an integral part of the steel plant complex. In 1967, coke ovens in the United States produced 63,775,000 tons of coke. One-sixth, or 92 million tons, of the total bituminous coal produced was charged to coke ovens. On the average, 1.43 tons of coal was required for each ton of coke produced.[71]

Conventional coking is done in long rows of slot-type ovens into which coal is charged through holes in the top of the ovens. The sidewalls or liners are built of silica brick, and the spaces between the chambers are flues in which fuel gas burns to supply the required heat. Each pound of coal carbonized requires 1,000 to 1,150 Btu and flue temperatures are as high as 2,700° F.[72]. The remaining heat in the partially spent combustion gases is accumulated in a brick checkerwork, which releases it to preheat the combustion air when the cycle is reversed. This is a typical regenerative cycle to conserve fuel and give a higher flame temperature.

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*This calculation is based on a specific gravity of 1.02 for blast furnace gas[64] (0.08233 pound per cubic foot). If an average value of 4.5 tons of blast furnace gas produced per ton of pig iron is assumed, then 109,300 cubic feet of blast furnace gas is produced per ton of pig iron, or 7,150,000 cubic feet for 65.4 tons, which is the average production per blast furnace per hour.[65] If an average value of 21 percent of the blast furnace gas having a Btu content of 90 is used to heat the stoves, then 135,180,000 cubic feet is used, or 65,590,000 cubic feet for each of the two stoves on heat. This amount to 13 pounds NO_x per hour, or 26 pounds per hour for the two stoves, or 114 tons per year.

The coal in the coking chambers undergoes destructive distillation during a heating period of about 18 hours. The noncondensable gaseous product is known as coke oven gas and on a dry basis has a heating value of about 570 Btu/cu ft. Approximately 35 percent of the coke oven gas produced is used in heating the oven.

The trend in new coke oven construction is toward higher ovens, 16½ to 19 feet as opposed to the usual 13 to 14 feet, which will increase coal throughput by 75 percent.[73] This increase is due in part to higher temperatures permitted by improved refractories and more uniform heating designs. This trend will tend to increase NO_X emission.

Actual analysis of two coke oven stack gas samples gave values of 41 to 50 ppm NO_X or an average of 45 ppm. In another test, an average of 28 ppm was obtained.[69]

It is estimated roughly that in the carbonization of 92 million tons of coal in the United States during 1967, more than 6,000 tons of NO_X was emitted.* This represents 0.23 percent of the estimated 1965 industrial NO_X emissions in the United States.[68]

7.4.2.3 *Miscellaneous Furnaces*

The cupola furnace is similar in many respects to the blast furnace. Its function is to melt scrap and pig iron for subsequent processing in steel production. Like the blast furnace, its offgas contains usable quantities of carbon monoxide which can be recovered and burned to preheat the air blast.[73]

The reducing conditions that tend to exist in the cupola furnace could not be expected to produce the quantity of NO_X that the high temperatures would suggest. Available data indicate a concentration of 13 ppm NO_X in the vent gases or 0.11 pound per ton of metal produced.[59] A questionnaire survey of 1,680 United States foundaries by the National Air Pollution Control Administration and the U.S. Department of Commerce shows that 14,600,000 tons of iron casting shipments was produced by cupolas in 1966. On this basis, iron cupolas emitted 805 tons of NO_X to the atmosphere during the year.

The basic oxygen furnace (BOF)

The use of air for bottom-blowing in the refining process for steel production has been common practice since 1870 but in recent years, it has declined to minor importance. The use of commercially pure oxygen for top-blowing has increased rapidly and this is now a major refining method. Bottom-blowing was characteristic of the Bessemer process, which is no longer used, whereas top blowing is characteristic of the basic oxygen furnace (BOF), the more common type today.[74]

The BOF method produces substantial amounts of carbon monoxide; and if this is permitted to burn off, some NO_X is produced by reaction of the very hot gas with air outside the furnace. One steel manufacturer gives a range of values of from 30 to 80 ppm or 0.36 to 1.0 pound NO_X per ton of steel. This can be avoided by use of a suitable hood system to collect the gas for other uses.[75] If these other uses include use as fuel, some NO_X may still be produced.

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* These calculations are based on a slot oven holding 20 tons of coal and provided with 30 separate heating flue combustion chambers. A heating period of 18 hours is assumed and a value of 1,100 Btu required to carbonize 1 pound of coal. This calculates to 81,000 Btu/flue/hr. When gas is burned at this rate, 0.005 pound of NO_X is produced per hour.[59] For 30 flues over 18 hours, 2.7 pounds of NO_X is produced, which is the amount produced in the carbonization of 20 tons of coal. For 92×10^6 tons, the NO_X production equals 6,210 tons.

Other furnaces using either regenerative or recuperative preheat of the combustion air, in addition to the open hearth, coke ovens and blast stoves are used for such lesser applications as reheating and soaking pit furnaces. Actual analysis of soaking pit stack gases has given average NO_x values of 25.8 and 21.5 ppm.[69] These values are in line with coke oven emissions (45.6 and 28.3 ppm) but considerably lower than open hearth values (243 and 320 ppm). NO_x emissions from soaking pit stack gases are estimated at 5,500 tons per year in the United States, based on 0.086 pound NO_x per ton of ingot steel production,[69] and U.S. ingot steel production of 127 million tons per year.[59]

Sintering operations are another NO_x emission source, differing somewhat from the conventional furnace. In this instance, finely divided iron-bearing material is mixed with a fuel such as coke breeze to give a product suitable for blast furnace use. The mixture is spread on a traveling grate and ignited by gas burners. The burning is continued by air drawn down through the grate. Analysis of stack gases from such sintering produces NO_x values of 47.2 to 36.3 ppm.[69] NO_x emissions from sintering stack gases are estimated at 27,000 tons per year in the United States, based on 1.04 pounds NO_x per ton of sinter[69] and sinter production of 51 million tons per year in the United States.[59]

7.4.3 Emissions

Emissions in the steel industry and its related processing have been concerned with fumes, smoke, and dust or particulates. The gases usually considered abnoxious have been SO_2, CO, and odors. The presence of oxides of nitrogen has been obscured by the heavy emission of particulates and a resulting lack of physical evidence. The NO_x emissions observed can be traced largely to the combustion of fuel oils and gas and, in part, to the burning of carbon monoxide, which is a product of the processing operations.

Planned equipment and processing changes for abatement of air pollution must consider NO_x emissions, e.g., higher temperatures increase NO_x production. On the other hand, the major shift now in progress from the open hearth to the basic oxygen furnace in steel production promises a substantial reduction in NO_x emissions. The NO_x produced in the BOF process is believed to result from the burning of the carbon monoxide produced in the operation and to some extent from the nitrogen content of the commercially pure oxygen used. This may be controlled by proper hooding and gas collection,[75] which may be a minor source of NO_x when used as fuel.

Regenerative type furnaces will be used in one capacity or another for some time, and may be modified for at least partial control of NO_x from combustion processes, as outlined in Section 4.1. In brief, these modifications emphasize avoiding excess air which limits the presence of one of the reactants in NO_x formation, regardless of the resultant increase in flame temperature.

Removal of NO_x from the products of combustion by scrubbing or adsorption have not as yet reached a stage of development which seems practical for metallurgical applications.

The use of electricity for heat in steel production is growing rapidly, and this transfers the NO_x emissions to the utility plant where easier control is expected. Projections to 1980 indicate that raw steel production will reach 180 million tons, of which 45 million (up from 13 million tons in 1967) will be produced in electric furnaces.[76]

Electric induction heating will reduce NO_x emissions at the furnace to the extent that fuel combustion is displaced. On the other hand, electric arc heating does produce NO_x. No quantitative data appear to be available, however.

The projected use of the plasma arc furnace[77] may produce a substantial amount of NO_x, and the related processes may require some form of inert blanketing if problems with air pollution are to be avoided.

7.4.4 Costs

No separate data are available for this industry on the costs of NO_x pollution control.

7.5 KILNS – CEMENT, LIMESTONE, AND CERAMICS

The kiln-type furnace is used in the production of cement clinker and quicklime and in the firing of ceramic-type products. The rotary kiln predominates the cement industry and is also extensively used for limestone calcining. However, the latter industry uses, to a considerable extent, the vertical shaft kiln both in its original form, which is gradually being retired, and the newer high-capacity design. For ceramic firing, the tunnel kiln is used for the smaller, more fragile items and the beehive kiln for larger items such as drainage pipe.

Cement clinker is produced by sintering intimately ground mixtures of limestone with suitable clays, shales, or marls. Such mixtures, either as dry feed or wet slurry, are gradually heated to sintering temperature (up to 2,900°F)[78] in rotary-type kilns. The product is a clinker which, when finely ground and mixed with a small amount of gypsum to control set, is the portland cement of commerce.

A rotary kiln is essentially a steel cylinder, varying in diameter from 8 to 25 feet and 150 to 700 feet long, lined with a refractory material. These kilns are slightly inclined and are rotated at about 1 rpm. Raw feed entering at the high end works its way gradually down to the lower end over a period of 2 to 4 hours. Preheated air, in excess, and fuel are fired at the lower end, so that the combustion gases travel countercurrent to the feed. During the slow travel of the feed down to the hot end of the kiln, a series of reactions takes place in a nonreducing atmosphere, ending in a partial melting. This sintered material is the cement clinker referred to above. The hot clinker is cooled by incoming combustion air that improves the overall thermal efficiency and gives a higher peak temperature.

The capacity of individual kilns has been increased in recent years to more than 10,000 barrels per day (376 pounds per barrel), but 2,000 to 6,000 barrels per day is representative of the industry.

In the United States in 1967, some 188 plants produced about 369 x 10^6 barrels of cement. Average fuel consumption in 1967 was 1.25 x 10^6 Btu/barrel or 6.66 x 10^6 Btu/ton of cement. The fuel consumed is shown in Table 7-12.

Limestone rock occurs in two principal variations. If it is almost entirely calcium carbonate ($CaCO_3$), it is known as a high calcium limestone. If a considerable portion of the calcium carbonate content is displaced with magnesium carbonate (from 30 to 45 percent), it is known as a dolomitic limestone. Either of these limestones, when heated, loses carbon dioxide (CO_2) to form quicklime.

At calcination temperatures of 1,700° to 2,450°F, dissociation of the limestone proceeds gradually inward from the outer surface of the stone particle. Temperatures in the higher range are required for dissociation to reach the center of the particle. Since a gradual temperature increase is preferred, the rotary kiln is particularly suited to limestone calcination. Product heat is recovered as preheat for the combustion air, as in cement kilns.

Table 7–12. FUEL CONSUMED BY CEMENT INDUSTRY IN U.S., 1967

Fuel	Amount consumed	Equivalent Btu, 10^{12}
Coal, 10^3 short tons	9,096	236
Oil, 10^3 bbl (42 gal/bbl)	4,956	30
Natural gas, 10^6 ft^3	159,717	196

Excessive heat is avoided if a high quality or active quicklime is desired. Longer heating at sintering temperature is required to produce dead-burned dolomitic lime for refractory furnace linings.

Vertical kilns were first used for limestone calcination, but these have been largely replaced with rotary kilns. However, a few new installations of vertical kilns of improved design have been announced.[79] The capacity limit, which was a major disadvantage, has been extended up to 500 tons per day, which is the equivalent of modern rotary kilns.

Vertical kilns are more thermally efficient than rotary kilns. Typical fuel consumptions are 5 x 10^6 Btu per ton[79] for vertical kilns and 7 x 10^6 for rotary.

The 1967 United States production of lime was 17,974,000 short tons in a total of 209 plants. Of this amount, 33 plants produced 63 percent of the total[80] Since fuel consumption statistics are not available for the manufacture of lime, a value of 6 x 10^6 Btu per ton was used to estimate the thermal requirements for limestone calcination in the United States in 1967 at 108 x 10^{12} Btu. No reliable breakdown as to the use of coal, oil, or gas appears to be available, but the literature suggests that a grandual switch to gas is in progress.

The ceramics industry embraces a multitude of products which include the more general headings of refractories, vitreous enamels, whitewares, abrasives, structural clay products, and ceramic minerals. The larger kilns used by the industry are of two types, tunnel and beehive.

The tunnel kiln varies from 2 to 10 feet wide and 4 to 8 feet high by 75 to 100 feet long. These kilns are gas- or oil-fired, with burners placed near the center of the tunnel. The material being fired moves slowly into the hot zone and is then cooled slowly in the remaining length of travel. Combustion air is introduced at the exit end and is preheated as it passes over the hotware leaving the kiln.

Beehive kilns are shaped as the name indicates and vary in size up to 60 feet in diameter. Burners are spaced around the periphery; combustion gases are diverted toward the dome, then down through the ceramic material stacked on the floor. Ducts under the floor lead the gases to a common stack, which usually serves four kilns.

7.5.1 Emissions

Particulates are the pollutants associated with cement, lime, and ceramic kiln operations. Limited data are reported in the literature on NO_x emissions from tunnel and beehive ceramic kilns, but no data have been found on NO_x from cement or lime kilns. Since large volumes of fuel are consumed and combustion air is preheated, significant NO_x formation would be anticipated in cement and lime kiln operations.

Estimated NO_x emissions from kiln operations in the U.S. during 1967 appear in Table 7-13.

Table 7–13. ESTIMATED NO_x EMISSIONS FROM KILNS IN UNITED STATES, 1967

Process unit	NO_x, tons/yr	Percent of total U.S. NO_x emissions
Cement kilns	108,000	0.8
Lime kilns	21,000	0.15
Ceramic kilns	21,000	0.15
Total	150,000	1.1

Cement and lime kiln emission estimates are based on the fuel consumptions discussed in Section 7.5 and on the correlation between NO_x production rate and heat input to the combustion unit[81] shown in Figure 8-1.

There are limited NO_x emission data for tunnel kilns used for firing ceramic items such as pottery. The results of five tests varied from 3 to 66 ppm with an average of 24 ppm.[82] Gas firing was used in all instances.

A large beehive kiln which can accommodate 1000 tons of ceramic ware requires a heat input of up to 15 x 10^6 Btu per hour.[82] Such a kiln, based on similar emission factors to those used above, will produce 2.2 pounds of NO_x per hour if gas fired and 4.8 if oil fired. If four kilns are served by a single stack, as is usually the case, the stack emission will be 8.8 pounds of NO_x per hour for gas and 19 for oil.

7.5.2 Control Techniques

The literature shows no references to commercial installation of equipment for removing NO_x from kiln waste gas or of modifications to kiln operations to reduce NO_x production. Water scrubbing is sometimes used for particulate removal from waste gas from lime kilns. In this operation, the gas contacts a slurry of calcium hydroxide, which should remove a 50/50 mixture of NO and NO_2 and reduce NO_x up to 20 percent (see Section 4.2.1). Flue gas recirculation, which is used to control temperature in some lime kilns,[83] should reduce NO_x emissions by lowering flame temperature.

Combustion gas in lime kilns contacts calcium oxide and calcium carbonate as it passes through the kiln, consequently, some NO_x probably reacts to form calcium nitrite and calcium nitrate.

The nitrites and nitrates would subsequently decompose in the high-temperature zone of the kiln, releasing any NO_x which had reacted. Thus, it is unlikely that contact between the combustion gas and lime or limestone in the kiln results in an overall reduction in NO_x emissions.

Several of the possible means of reducing NO_x emissions in kiln operation are the same as in the high-temperature combustion discussed in detail in Section 4.1. These include:

1. Conversion to oil and preferably to gas firing. However, advantage should be taken of the economic aspects of an intermittent gas supply by retaining an alternate firing means.
2. Keeping excess air to a minimum.
3. Automatic control of firing variables.
4. Modification of firing design such as burner location.
5. Avoiding peak flame temperature to the extent the process permits.

Electric heating eliminates all the pollutants associated with combustion sources, but its use in kiln operations is very limited. Another means of emission control in kiln operation is the choice of kiln type. Some NO_x reduction in limestone calcining is obtained by using a vertical instead of a rotary kiln, but only because less fuel is consumed.[51] The higher thermal efficiency, lower capital and operating costs, and increased capacity of recently designed vertical kilns may result in a long-term trend away from rotary kilns.

Scrubbing as a means of NO_x reduction is not as yet feasible for combustion gases. Section 4.2 describes the progress that has been made in this area.

7.6 GLASS MANUFACTURE

The glass manufacturing industry is made up of several basically different types of operation. They are:

1. Glass container manufacture.
2. Fiber glass manufacture.
3. Flat glass manufacture.
4. Specialty glass manufacture.

The raw materials used in glass manufacture consist primarily of silica sand, soda ash, limestone, and cullet (crushed waste glass). In the production of window and plate glass, for example, temperatures in the range of 2750° to 2850°F may be required to melt these raw materials into a viscous liquid.

The furnaces used are of the pot type if only a few tons of a specialty glass are to be produced, or of the continuous tank type for larger quantities. By far the larger amount of glass is melted in furnaces, and only these will be considered in connection with NO_x control.

Continuous tank furnaces have a holding capacity of up to 1400 tons and a daily output of as much as 300 tons. Figure 7-14 is a cut-away view of a typical side-port, regenerative container glass furnace.[84] It is also representative of some specialty glass furnaces. The "batch" feed is introduced at the left, or "melting end," which is maintained at as high a temperature as the production requires. The glass is heated by direct radiation from the flames and the refractory melter crown. As the mass fuses, it passes into the "fining zone" and finally through the submerged

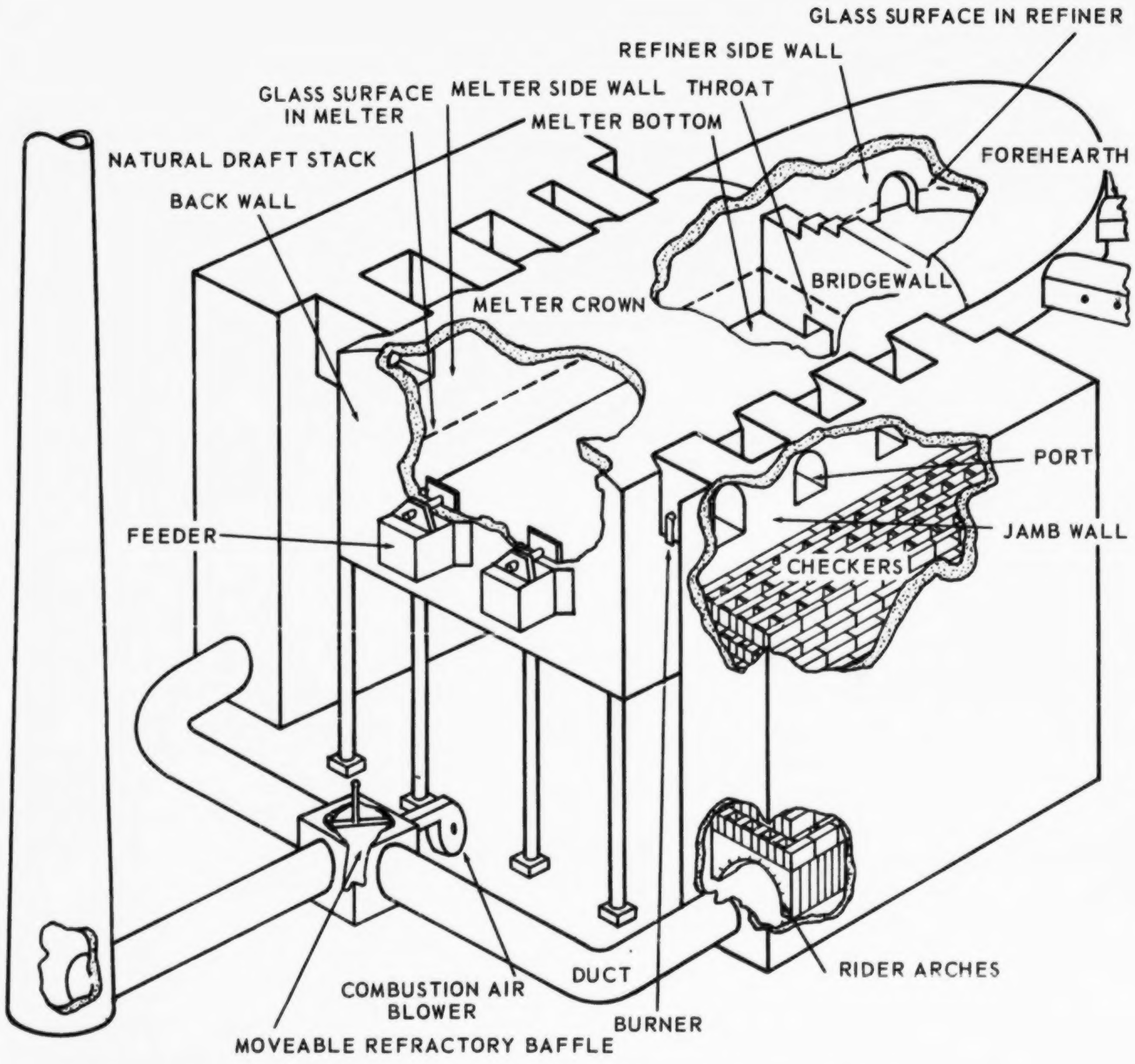
GLASS SURFACE IN REFINER
REFINER SIDE WALL
GLASS SURFACE IN MELTER
MELTER SIDE WALL
THROAT
MELTER BOTTOM
NATURAL DRAFT STACK
FOREHEARTH
BACK WALL
BRIDGEWALL
MELTER CROWN
PORT
JAMB WALL
FEEDER
CHECKERS
RIDER ARCHES
DUCT
COMBUSTION AIR BLOWER
BURNER
MOVEABLE REFRACTORY BAFFLE

Figure 7-14. Regenerative side port glass-melting furnace.

throat of the bridgewall into the "working zone."

The combustion gases, on leaving the melting zone, retain a considerable amount of heat. This is reclaimed in a regenerator or brick checker chamber. When the firing cycle is reversed, combustion air is preheated by being passed through the brick work. Preheating saves fuel but increases the flame temperature.

A variation on side-port firing is the end-port fired furnace, in which a single burner replaces multiple burners at one end of the tank. It is possible that the different type of firing could influence NO_X emission. The combustion gases follow a U-shaped path and enter a checker chamber for heat reclamation. Reversal of the cycle is then similar to that in side-port firing. Numerous variations on construction and firing include direct firing, and regenerative, with end point firing.

Coal is not used in glass melting. Since molten glass is conductive, heating is used as a booster to supplement fuel firing whenever technically and economically practical. Gas and, to a lesser extent, fuel oil are the preferred fuels.

7.6.1 Emissions

The flue gas from glass-melting tanks is the major source of NO_X emissions in the glass industry. The operation of these tanks is similar to that of open-hearth furnaces used in steelmaking; regenerative checkerwork sets absorb heat from the combustion gases for subsequent release to the incoming combustion air. This is accomplished by a reversing valve which puts each checkerwork set through its heating and cooling cycle in turn. The sequence of intense high-temperature combustion and quenching in the checkerwork sometimes raises NO_X emission to levels perhaps fivefold those experienced in a steam boiler of equivalent heat release. This observation is based on measured emissions of 0.87 pound NO_X per million Btu fired for glass-melting tanks firing an average of 38 million Btu of gas per hour[60] compared to 0.13 pound NO_X per million Btu of heat input for gas firing in normal combustion equipment of this size (see Figure 8-1).

Normal combustion supplies the lesser amounts of heat used in glass annealing and tempering, so that these processes are only minor sources of NO_X.

Annual NO_X emissions from the United States glass industry are roughly estimated at 110,000 tons for 1967, or about 1.3 percent of total NO_X pollutants. This is based on reported fuel usage in 1962,[86] and reported glass production for 1962 and 1967.[87] A 300-ton-per-day glass melter, currently the largest size, will consume about 92 million Btu per hour of fuel and discharge an estimated 80 pounds per hour of NO_X, based on an emission factor of 0.87 pound per million Btu of fuel fired. This factor is taken from results of tests run in Los Angeles on glass-meter stack gas containing NO_X concentrations ranging from 435 to 1,320 ppm, with an average of 570 ppm.[60]

The type of furnace and firing shown in Figure 7-14 is reminiscent of that used in producing steel by the open-hearth furnace. Actual chemical analyses of the stack gas from an open-hearth furnace fired with 70 percent gas and 30 percent oil varied from 500 to 800 ppm of NO_X, with an average of 700 ppm. Similar results were found for four glass furnaces. The values ranged from 435 to 1,320 ppm, with an average of 570 ppm.[60] Other analyses of exhaust gases from a large, regenerative, gas-fired furnace showed 137 ppm of NO_X when amber glass was melted and 725 ppm when flint glass was melted.[84]

7.6.2 Control Techniques

Controls for NO_X emissions have not been developed for the glass industry. Combustion modifications for reducing flame temperatures do not appear applicable, since high flame temperatures are required to heat the charge to the 2,600° to 2,850°F temperatures required in glass melting. Operation with excess air might lower NO_X levels while maintaining or increasing temperature; it would require improved controls. Automatic controls and changes in burner positioning are potential methods of reducing NO_X.

Control measures which may be specific to glass melting are:

1. Minimize hot spots within the furnace. It is known that minute changes in residence time in extremely high temperature zones can considerably affect NO_X emission. Table 3-1 illustrates the situation.
2. Use an end-fired tank which has a single large burner and a long path travel. A large, luminous flame is known to produce less NO_X than an intense restricted flame; a tank with such a burner might produce less NO_X.
3. Use electric heating as a booster source when high temperature or increased production is desired. It is favored for colored glasses and tends to extend refractory life. An all-electric melter requires less capital investment than conventional melters.[88] Of importance from the pollution standpoint, electric heating reduces NO_X emission to the extent, at least, that combustible fuels have been displaced. However, the economics involved are not clearly in favor of

electric heating except as a "booster," since for most locations power is a more costly source of energy than fuel, even though power is 75 percent efficient and fuel only 15 to 20 percent.[89] The use of power transfers NO_x emissions to the power plant.

High temperature flames, particularly those enriched with oxygen, are the source of high levels of NO_x emissions. Consequently, small room-scale or laboratory operations[90] which use high temperature, oxygen fortified flames–such as bench-type glass-blowing and quartz-working and flame photometry–are potentially sources of high levels of NO_x.

7.7 MISCELLANEOUS NO_x EMISSION SOURCES

7.7.1 Process Description

7.7.1.1 Refractory Fibers

The production of fibers such as mineral and glass wool requires the melting of refractory material (300°F). The molten material is reduced to a stream of globules by passage through a strong blast of highly superheated steam or air. The flying molten globules develop and trail long fibrous tails.[91] Although much more is involved, this is the way rock wool and similar mineral fibers are produced. Once assembled into batts, etc., the material is widely used for insulation purposes. Eight to 10 million pounds of alumina-silica fibers are produced each year.[92]

No specific data are available on the NO_x emitted during fiber production.

7.7.1.2 Perlite Expanding Furnaces

Perlite is a glassy volcanic rock which occurs as spherical particles. When perlite is heated rapidly, the water which the spherules contain causes them to puff up or expand into a white cellular low density material.[93] In 1967, some 357,560 tons of expanded perlite were produced,[94] of which roughly 90 percent was used as an aggregate in plaster and concrete. Essentially all furnaces used to expand perlite are heated with natural gas. The temperature required is in the range of 1,450° to 1,800°F. A value of 19 ppm of NO_x has been found in the exhaust gases of one furnace.[95]

7.7.1.3 Baking and Drying Ovens

Ovens for baking and drying are used diversely as bakery ovens, sand core ovens for foundries, paint baking ovens, plastic curing ovens, and rock wool drying ovens.[96] These may be direct-fired, in which case the combustion products are in contact with the material being heated; or indirect-fired, in which case air is heated and then circulated through the oven.

Baking and drying ovens vary considerably in size, design, and construction. Although some are oil-fired, gas-firing is usually preferred. The combustion air need not be preheated since operating temperatures are usually in the range of 180° to 650°F. Combustion gases are discharged directly to the atmosphere unless they contain fumes that require the use of an afterburner. Although a relatively large number of such ovens may be in use, their average hourly heat requirement of perhaps 1.2 million Btu is low. NO_x stack emission has been reported to be 10 to 40 ppm.[95]

7.7.1.4 Spray Dryers

In spray drying, a highly dispersed liquid is brought in contact with a high temperature gas. The hot gases are usually obtained from a direct-fired gas or oil heater. If a controlled atmosphere is necessary, indirect heating is required. A cyclone separator or a baghouse is frequently used to separate the dried product from the hot gases.[97]

The detergent industry is a large user of spray dryers. The heat requirement of such dryers is about 15 million Btu per hour, and the NO_x content of the stack gas has been reported to be about 7 ppm.[95]

7.7.1.5 Welding

The high temperatures involved in electric arc and oxyacetylene welding (3,500°F) are expected to favor NO_x production. Measurements made under conditions of restricted ventilation have shown that amounts of NO_x

vary from a trace to nearly 35 ppm, depending on the particular operation and the conditions involved. These samples were taken from the visible fume stream at a distance of 6 inches from the arc.[98] It is estimated that welding operations in the United States contribute roughly 70 tons of NO_X per year to the atmospheric burden. This estimate is based on three assumptions: that the mean gas flow in all welding is 10 cubic feet per minute, that the concentration of NO_X is 10 ppm, and that data from Los Angeles are representative of the United States at large.

Welding operations in which no visible emissions exist should not be assumed to be free of NO_X.

7.7.1.6 Electrostatic Precipitators

Electrostatic precipitators are used extensively to remove very small particulate material from gases. The equipment essentially consists of a series of electrodes which, because of their high voltage (20,000 to 100,000 volts in single-stage units) create a corona discharge that ionizes gas molecules and electrically charges the particles passing through the field. The charged particles then tend to migrate toward oppositely charged surfaces and are removed from the gas stream. It is suggested that the corona discharge forms ozone and atomic oxygen, which can react with nitrogen to form nitrogen oxides.

Certain data from precipitators tied to coal-fired steam boilers indicate that such formation of NO_X does occur; other equally acceptable data show a decrease in NO_X on passage through an electrostatic precipitator. This marked disagreement in results has not been explained, and additional information of interest may be developed by further research.

Until more reliable information is available, one cannot consider electrostatic precipitation a contributor to NO_X.

7.7.1.7 High-Level Exposure in Agriculture

A noncombustion source of nitrogen dioxide is the gas formed in silos in the first few days after filling.[99] Anaerobic bacterial action occurring in the green fodder produces nitrogen dioxide in quantities sufficient to impart a readily visible color. Such a concentration is expected to exceed 40 ppm, if an assumed path of 5 feet is used in the formula for minimum visibility: 2,400 divided by the path length in inches = ppm NO_2.[100] Thus, silage gas constitutes a high level point source of the highly toxic oxide of nitrogen (NO_2).

7.7.2 Control Techniques

The first of the combustion sources described above (Section 7.7.1.1) involves the use of very high temperatures for the production of refractory fibers. Both cupola- and reverberatory-type furnaces are used. These furnaces are extensively used in the manufacture of steel, and control of these NO_X emission resulting from the combustion of fuel has been described in Section 7.4.2. Probably the most practical control is to use as little excess air as possible. In addition to partially controlling the nitrogen oxides, the low-excess-air technique will provide the highest flame temperature. Also to be avoided are highly turbulent flames or at least local areas of high turbulence which produce extremely high local temperature. (See Section 5.2 for a more detailed description.) In general the long nonturbulent flame is to be preferred to minimize NO_X emission.

The next three heating operations (perlite expanding furnaces, baking and drying ovens, and spray dryers) require only moderate temperatures. Under these circumstances, control measures can be adopted which would otherwise be impossible if very high temperatures were required. Such control of the combustion process has been described in detail in Section 4.1. Control of excess air to the combustion zone is probably the most practical approach for partial NO_X reduction. Other approaches are the use of two-stage combustion and flue gas recirculation and the avoidance of flame turbulence. The present technology does not provide for complete removal of all NO_X on a practical basis. The status of such endeavors is the subject of Section 4. In most cases, particulate and fume control have been the dominant air pollution problems. All control and process variables are interrelated, however, and in new construction, particularly, NO$_X$ control can be an integral consideration.

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8. NITROGEN OXIDES EMISSION FACTORS

For an accurate air pollution survey, whether for a single source or for a metropolitan area, pollutant emissions must be identified by type and quantity. This determination–together with meteorological, air quality and effects sampling programs, and strong enforcement actions–fulfills the requirements for local, state, and Federal air pollution control activities.

An adequate emission investigation will provide evidence of source emissions and will define the location, magnitude, frequency, duration, and relative contribution of these emissions. This emission survey of pollutants will include the determination of emission rates from fuel combustion at stationary and mobile sources, from solid waste disposal, and from industrial process losses.

Ideally, the determination of emission rates should include a stack analysis of all sources of interest, but this is impractical when an air pollution survey must cover a large land area that could contain many thousands of sources. Emissions must be estimated for sources that do not have accurate stack gas analyses. Estimates are arrived at by the use of emission factors, which are estimates of pollutant emission rates based on past stack sampling data, material balances, and engineering appraisals of other sources similar to those in question.

8.1 EMISSION FACTOR ACCURACY

The accuracy of emission estimates depends upon the use of an accurate fuel quality figure as well as an accurate emission factor. It is important to recognize, however, that the development of accurate NO_X emission factors is very difficult because of the complex nature of nitrogen oxide formation from combustion processes.

There is no convenient way of anticipating the approximate amount of NO_X pollutants formed from a given amount of fuel, as there is for the oxides of sulfur. The formation of SO_X is directly related to the concentration of sulfur in the fuel. On the other hand, NO_X can be formed in substantial concentrations of several hundred ppm or more with no chemically bound nitrogen in the fuel; e.g., in natural gas combustion (see Section 4.1).

The amount of NO_X emitted depends upon equipment design, a complex set of combustion conditions, and operating variables such as installation size, type of burner, cooling surface area, firing rate, and air/fuel ratio. Consequently, the determination of accurate emission factors that represent average or typical emissions from each class of equipment involves a complicated sampling procedure, which requires the selection of representative equipment and testing under representative operating conditions. The quotation below, taken from Report No. 3 of the Joint Los Angeles County report[1] concerns NO_X emissions from the single most important emission source, steam power plants, and succinctly illustrates these problems.

"In the determination of an NO_X emission factor for power plants, some 130 tests including 554 individual samples were considered. The Department of Water and Power of the City of Los Angeles has been making an extensive study of the effect of operating variables on NO_X emissions. These studies have included a testing program in which two to three tests per week were performed for a period greater than a year.

"The rates of emission of NO_x from units as complex as these, with the possibility of a number of constantly fluctuating operating variables, may be assumed to be constantly fluctuating also. In these circumstances, the rate of emission of NO_x at any given instant in any plant may be different from the rate of emission at the next instant. Experience gained during the carrying out of the project has shown these assumptions to be true. A striking example of this variability is the fact that samples taken as nearly at the same time as possible from two probes in close proximity to each other as possible show two different values for NO_x concentrations. It was found that actual rates of NO_x emission from sister units may be different for operating conditions which are the same for each unit within the limits of ability to determine. This phenomenon has been verified repeatedly.

"Thus, it may be seen that in the development of an emission factor, calculations must be based on averages of many data taken under many different conditions. As pointed out in the discussion of asphalt paving plants, the use of such a factor to determine the rate of NO_x emission from a single unit at any given time may produce data which are far from reliable for the conditions existing at that time.

"During the carrying out of the test program on power plant boilers, a number of phenomena were brought to light. Instead of clarifying the situation, many of these observations served merely to point up the complexity of the problems. It should be borne in mind that the examples and curves shown are in each case for some particular unit and should not be construed to be correction factors for measured emission rates from any other unit. The degree and direction of the effect of operating variables upon NO_x production must be determined individually for each particular unit to be considered."

The study cited was a joint Federal, state, county, and industry project in which Mills et al. measured NO_x emissions from a wide variety of gas- and oil-fired combustion equipment, ranging from domestic heaters to large steam boilers, and were able to establish the general relationship between gross heat input and NO_x (as NO_2). The experimental data they obtained are in many cases the best or the only actual measurements reported in the literature. Their data are reproduced in Figure 8-1.[1] Note that in Figure 8-1, the average heat input includes gross heat in the fuel plus heat contained in the preheated combustion air. All data given are for combustion processes taking place at or near standard pressure of 1 atmosphere.

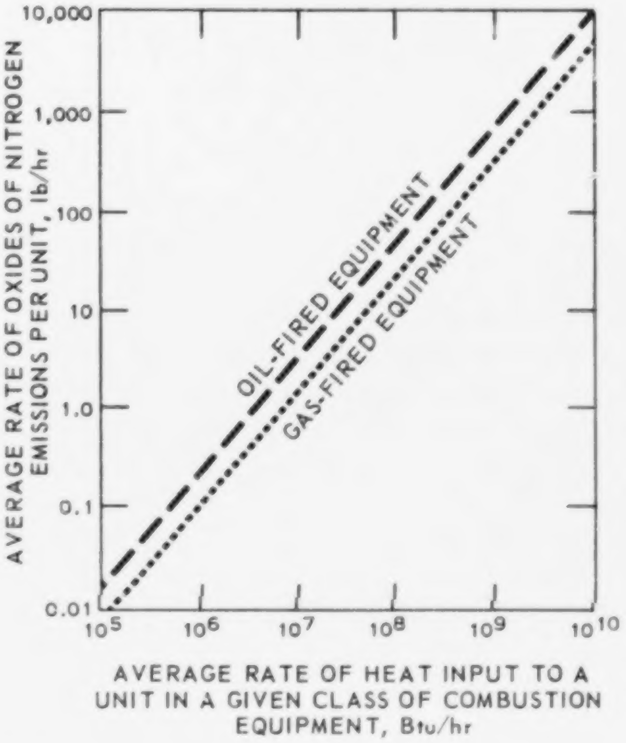

Figure 8-1. Estimation of average unit oxides of nitrogen emissions from similar combustion equipment.[1]

Wide variations from these curves are to be expected for individual units, depending upon specific fuels, operating conditions, and equipment design. The top end of the curves is not valid for some measured cases (above about 2 x 10^9 Btu/hr). However, rough estimates of NO_x emissions from a variety of combustion equipment can be made from these curves if the fuel combustion rate is known. NO_X emission factors from these and other sources have been compiled by Duprey.[2]

Emission factors have been used, for the most part, to represent *average* emission rates for a particular type of fuel for a particular consumption sector. If no adjustments are made in these factors for specific changes in type and size of equipment, operating rates, and control equipment over a certain period, the factors may not represent current emissions.

In some instances, emission factors used in this document do not agree with those published by Duprey.[2] Such differences have been noted and explained in the description of emission factors for catalytic cracking regenerators and CO boilers in Section 7.3; the emission factors for open burning appear questionable, as discussed in Section 6.2. In other instances, emission factors were derived from published or unpublished data if no published emission factors were found. Thus, emission factors were derived for cement and lime kilns in Section 7.5, and for iron ore sintering, coke ovens, and steel soaking pits in Section 7.4.

Table 8-1 is a compilation of average emission factors for NO_X from various types of sources. These emission rates represent uncontrolled sources unless otherwise noted. For an operation in which control equipment is

Table 8–1. EMISSION FACTORS FOR NITROGEN OXIDES DURING COMBUSTION OF FUELS AND OTHER MATERIALS

Source	Average emission factor
Fuels	
Coal	
Household and commercial	8 lb/ton
Industry	20 lb/ton
Utility	20 lb/ton
Fuel oil	
Household and commercial	12-72 lb/10^3 gal
Industry	72 lb/10^3 gal
Utility	104 lb/10^3 gal
Natural gas	
Household and commercial	116 lb/10^6 ft^3
Industry	214 lb/10^6 ft^3
Utility	390 lb/10^6 ft^3
Wood	11 lb/ton
Combustion sources	
Gas Engines	
Oil and gas production	770 lb/10^6 ft^3
Gas plant	4,300 lb/10^6 ft^3
Pipeline	7,300 lb/10^6 ft^3
Refinery	4,400 lb/10^6 ft^3
Gas Turbines	
Gas plant	200 lb/10^6 ft^3
Pipeline	200 lb/10^6 ft^3
Refinery	200 lb/10^6 ft^3
Waste Disposal	
Open burning	11 lb/ton
Conical incinerator	0.65 lb/ton
Municipal incinerator	2 lb/ton
On-site incinerator	2.5 lb/ton

Table 8–1 continued. EMISSION FACTORS FOR NITROGEN OXIDES DURING COMBUSTION OF FUELS AND OTHER MATERIALS

Source	Average emission factor
Other combustion	
Coal refuse banks	8 lb/ton
Forest burning	11 lb/ton
Agricultural burning	2 lb/ton
Structural fires	11 lb/ton
Chemical industries	
Nitric acid manufacture	57 lb/ton HNO_3 product
Adipic acid	12 lb/ton product
Terephthalic acid	13 lb/ton product
Nitrations	
large operations	0.2-14 lb/ton HNO_3 used
small batches	2-260 lb/ton HNO_3 used

utilized, the emission rate given for an uncontrolled source must be multiplied by: 1 minus the percent efficiency of the equipment, expressed in hundredths. Emission factors are from a Public Health Service Publication,[2] a study contract,[3] and an emissions survey.[4]

Examples of how to use emission factors are given below.

1. Fuel oil combustion.

   Given: Power plant burns 50,000,000 gal of fuel oil per year.

$$50{,}000{,}000 \times \frac{104}{1000} = 5{,}200{,}000 \, \frac{\text{lb } NO_X}{\text{yr}}$$

2. Solid waste disposal.

   Given: Conical incinerators burns 7,000 tons of waste per year.

$$7{,}000 \times 0.65 = 4{,}550 \, \frac{\text{lb } NO_X}{\text{yr}}$$

3. Process industries.

   Given: A certain large continuous nitration employs 40 tons per day of strong HNO_3. If the control device is 90% efficient, what is the daily evolution of NO_X? (EF = emission factor.)

If EF = 12 lb/ton HNO_3 used, then

$40 \times 12(1.0 - 0.9) = 4.8$ lb NO_X/day

8.2 REFERENCES FOR SECTION 8

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9. POSSIBLE NEW TECHNOLOGY

Besides the demonstrated and promising techniques for controlling nitrogen oxide emissions from combustion discussed in Sections 4 and 5, several methods appear to have potential, but have not yet been proved.[1]

9.1 POTENTIAL COMBUSTION MODIFICATIONS

9.1.1 Oxygen Enrichment

Oxygen enrichment is becoming increasingly more practical as pure oxygen becomes less expensive because of its large-scale use in industry, particularly in the steel industry. In the glass industry (see Section 7.6.2), oxygen addition is sometimes cheaper than electrical heating to boost furnace capacity. As a method of NO_x control, the use of pure oxygen in the flame gives a higher flame temperature and therefore tends to produce more NO_x, not less; this effect prevails until the oxygen supply is so pure that there is not enough N_2 left in the flame to produce NO_x. Commercial oxygen that is 70 percent O_2 and 30 percent N_2 is probably not pure enough to accomplish this result. If furnace operation with enriched oxygen is to become practical, it will be necessary to redesign the heat recovery system to make up for the lack of unburned nitrogen gas as a heat carrier. This will require substantial developmental research, and the net effect on NO_x emissions is not now predictable.

9.1.2 Fluid Bed Combustion

Fluid bed combustion has been amply demonstrated as an effective means to even out high spot temperatures in the combustion zone of petroleum catalytic crackers. The application of this technique to the combustion of pulverized coal was expected to give less NO_x, but preliminary results failed to show the expected decrease. The large amounts of chemically bound nitrogen in coal are a possible contributing factor (see Section 4.1.3.3).

If this problem can be overcome, development work on a new boiler design can proceed, taking into account the fact that the burning section must be much larger than at present to allow a maximum fluidizing gas velocity of 5 to 6 feet per second versus present furnace gas velocities of 60 feet per second. The boiler section can be much smaller than at present because of the greatly improved rates of heat transfer in a fluid bed.

9.1.3 Centralization of Energy Source

Electric boilers and central power are becoming increasingly more practical for domestic and commercial space heating as urban concentration increases. The use of direct electric heating and the potential use of waste heat from utility power plants have already been discussed. A logical extension of that discussion would be the consideration of (1) the applicability of the use of electric boilers to produce steam for heating, (2) the distribution of a superheated water supply from a central power plant, or (3) the use of a circulating heat carrier, such as Dowtherm, that could supply individual flash boilers in a large apartment of industrial complex. These alternatives are all subject to the same parameters of power costs and the same parameters involved in the substitution of a large utility plant, where problems of air and water pollution would be centralized rather than spread out over many smaller units.

9.2 FLUE GAS REMOVAL

Selective reduction of NO_x by ammonia over supported platinum catalyst has already been discussed in Section 4.3 in connection with the content of nitric acid stack-gas emissions. Such reduction has been used in three nitric acid plants with very limited success.

The use of noble metal catalyst restricts the application of this technique to gases containing 1 ppm or less sulfur oxides.

Only the flue gas from gas-fired equipment could possibly meet this requirement, since no gas desulfurization process can be expected to provide such complete SO_2 removal.

The use of metal catalysts other than noble metals for the selective ammonia reduction of NO is discussed in several patents.[2-4] References *3* and *4* indicate that these catalysts are not sensitive to sulfur poisoning. If these claims are correct, NH_3 reduction could be used in coal- and oil- as well as gas-fired plants. Considerable research would be needed, however, before such a speculative system could be developed.

9.2.1 Improved Aqueous Scrubbing

In Section 4.2, it was indicated that lime-water scrubbing removes about 20 percent nitrogen oxides. Such removal is believed to be in the form of N_2O_3 produced by the interaction of NO and NO_2 in equal molar quantities; this removal could perhaps be improved by increasing the NO_2/NO ratio from its present flue-gas value of about 0.1 to a level of 1.0. Techniques that have been suggested[1] for achieving the more optimum NO_2/NO ratios include catalytic oxidation, homogeneous oxidation with ozone, and addition of NO_2 to the gases. In the case of NO_2 addition, part of the NO_2 might be obtained from the nitrites and nitrates formed in the scrubber by thermally decomposing these salts and oxidizing the concentrated NO_x produced.

9.3 REFERENCES FOR SECTION 9

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SUBJECT INDEX

A

Agriculture, high level exposure in, 7-43
Air combustion, low excess, 4-5–4-6
Ammonium nitrate manufacture, 7-12

B

Baking and drying ovens, 7-42
Basic oxygen furnace, 7-35
Blast furnace, 7-32
Boilers
  [See: Coal-fired boilers; Electric power plant boilers; Packaged boilers]
Burner configuration, 4-8
Burner Location and spacing, 4-8–4-9

C

Coal-fired boilers, limitations, 5-4
Coal refuse fires, 6-6
Coking ovens, 7-34
Combustion equipment (small), 4-11
Combustion modification, 4-1–4-3, 9-1
Combustion processes (large fossil fuel), 5-1–5-11
Commercial heating, 6-1–6-3
Control processes, potential, 4-13
Costs
  [See: Electric power plant boilers' Engines (stationary); Incineration and other burning; Industrial and chemical processes; Nitric acid manufacture; Organic oxidations; Organic nitrations; Petroleum and natural gas industries; Metallurgical processes]
Cupola furnace, 7-35

D

Definitions, 2-1
Design modifications, 4-8
Diesel engines, 5-10
Domestic heating, 6-1–6-3

E

Electric power plant boilers, 5-5
Electrostatic precipitators, 7-43
Emission factor accuracy, 8-1
Emissions, factors affecting, 4-3, 7-1
Emissions in United States, 3-1–3-2
Engines (stationary), 5-5–5-11
  [See: Diesel engines; Gas engines; Piston engines; Turbine engines]
Explosives manufacture and use, 7-21

F

Fertilizer, 7-24
Flue gas cleaning, 4-11, 9-1
Flue gas recirculation, 4-6–4-7
Fluidized bed combustion, 4-9, 9-1
Forest wildfires, 6-5
Formation of nitrogen oxides, 3-1–3-5
Fuel type and composition, 4-3
Furnaces
  [See: Basic oxygen furnaces; Blast furnace; Cupola furnace; Glass melting furnace; Open hearth furnace; Perlite expanding furnaces]

G

Gas engines, 5-11
Glass manufacture, 7-39
Glass melting furnace, 7-39

H

Heat release and transfer rates, 4-4

I

Incineration and other burning, 6-3
Industrial and chemical processes, 7-1

K

Kilns, 7-37

L

Lead chamber process, modified, 4-13–4-14
Limestone wet-scrubbing process, 4-11

M

Metallurgical processes, 7-32
Metals pickling, 7-25

N

Nitric acid manufacture, 7-2
Nitric acid uses, 7-11–7-25

O

Open hearth furnace, 7-34
Operating conditions, modification, 4-5
Organic nitrations, 7-14
Ovens
  [See: Baking and drying ovens; Coking ovens]

P

Packaged boilers, 5-4–5-5
Perlite expanding furnaces, 7-42
Petroleum and natural gas industries, 7-25
Piston engines, 5-5–5-9
Possible new technology, 9-1

R

Refractory fibers, 7-42

S

Scrubbers
  [See: Limestone wet-scrubbing process; Lead chamber process, modified]
Sintering operations, 7-36
Sources of nitrogen oxides, 3-1–3-5
Spray drying, 7-42
Stack gases, composition and solubility of, 4-12
Steam and water injection, 4-7
Steel production, 7-34
Structural fires, 6-6

T

Turbine engines, 5-9

V

Vegetation burning, controlled, 6-5

W

Waste disposal, 6-4
Welding, 7-42
West-scrubbing process
  [See: Limestone wet-scrubbing process]